Two-Dimensional Transition Metal Carbides

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ABSTRACT

Herein we report on the synthesis of two-dimensional transition metal carbides and carbonitrides by immersing select MAX phase powders in hydrofluoric acid, HF. The MAX phases represent a large (>60 members) family of ternary, layered, machinable transition metal carbides, nitrides, and carbonitrides. Herein we present evidence for the exfoliation of the following MAX phases: Ti3AlC2, Ta4AlC3, (Ti0.5,Nb0.5)2AlC, (V0.5,Cr0.5)3AlC2, and Ti2AlCN by the simple immersion of their powders, at room temperature, in HF of varying concentrations for times varying between 10 and 72 h followed by sonication. The removal of the “A” group layer from the MAX phases results in 2-D layers that we are labeling MXenes to denote the loss of the A element and emphasize their structural similarities with graphene. The sheet resistances of the MXenes were found to be comparable to multilayer graphene. Contact angle measurements with water on pressed MXene surfaces showed hydrophilic behavior.

KEYWORDS: MXene • two-dimensional materials • carbides • carbonitrides • exfoliation

Such high decomposition temperatures, however, induce recrystallization and the Mn+1Xn layers turn into nonlayered, bulk 3-D cubic carbides and/or nitrides with rock-salt structures with some ordering of the vacancies on the X sites.25–27

It is important to note that the bonding in the MAX phases is a combination of metallic, covalent, and ionic bonding, and the bonding strength is, in most cases, quite strong.25

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Our first attempt to exfoliate MAX phases was carried out by immersing Ti$_3$AlC$_2$ powders in 50% hydrofluoric acid, HF, at room temperature for 2 h. This procedure resulted in the selective etching of the aluminum, Al, layers and their replacement by hydroxyl, OH, and fluorine, F, surface groups. Besides nanosheets, we also observed scrolls, nanotubes, and multilayers of Ti$_3$C$_2$ after sonication. In that work, and given that over 60 MAX phases are known to exist, we speculated that Ti$_3$C$_2$ could very well represent a member of a much larger family of 2-D transition metal carbides and/or nitrides. To emphasize their similarity to graphene, we proposed to label these 2-D solids "MXenes".

The purpose of this paper is to show that indeed it is possible to exfoliate a number of chemically quite diverse, Al-containing MAX phases. In all cases, the operative reactions are presumed to be

$$M_{n+1}AX + 3HF = AlF_3 + M_{n+1}X_n + 1.5H_2 \quad (2)$$

$$M_{n+1}X_n + 2H_2O = M_{n+1}X_n(OH)_2 + H_2 \quad (3)$$

$$M_{n+1}X_n + 2HF = M_{n+1}X_nF_2 + H_2 \quad (4)$$

The following MAX phases were chosen for study: Ti$_2$AlC, Ta$_3$AlC$_3$, Ti$_3$AlCN, (V$_{0.5}$,Cr$_{0.5}$)$_3$AlC$_2$, and (Ti$_{0.5}$,Nb$_{0.5}$)$_2$AlC, henceforth referred to as TiNbAlC. The first two were chosen to show that it is possible to exfoliate both M$_2$AX (211) and M$_3$AX$_3$ (413) phases, in addition to the already exfoliated M$_3$AX$_2$ (312) phase. The (V$_{0.5}$,Cr$_{0.5}$)$_3$AlC$_2$ and TiNbAlC compositions were chosen to show that the M element needs neither to be confined to Ti nor be a single element; Ti$_3$AlCN was chosen to show that the X element need not be confined to C but can also be a mixture of C and N.

RESULTS AND DISCUSSION

The HF treatment process yield, $Y$, was obtained by measuring the initial powder weight before HF treatment ($W_i$) and the weight, $W_f$, after HF treatment (i.e., after several iterations of washing and subsequent drying). $Y$ was then calculated to be the ratio $W_f/W_i \times 100\%$. We note that the values reported in Table 1 are, thus, most likely lower than the actual synthesis yields because some powder is inevitably lost in the washing steps.

The structures before and after HF treatment were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The MXene sheets were investigated using transmission electron microscopy (TEM) and optical microscopy (OM). The resistivity and contact angle measurements were carried out on cold pressed discs (shown in Figure 2) of HF-treated powders.

The starting Ti$_2$AlC powders (Figure 3A-a) contain small amounts of Ti$_3$AlC$_2$ and TiC as secondary phases, which were estimated to be <5 wt % by Rietveld analysis. Figure 3A-b shows the XRD pattern of the HF-treated powders. Figures 3A-c and A-d show, respectively, the diffractograms of the HF-treated and as-received powders after cold pressing. Figure 3B-a shows the corresponding results for Ta$_3$AlC$_3$ and Figure 3C those for TiNbAlC. The results for (V$_{0.5}$,Cr$_{0.5}$)$_3$ AlC$_2$ are shown only as an inset in Figure 3C for brevity's sake and because the exfoliation protocol did not...
result in the total conversion of the compound to its corresponding MXene. The XRD results for Ti3AlC2, before and after HF treatment, are shown in Figure 3D.

A perusal of the XRD results depicted in Figure 3 clearly demonstrates a drastic loss in crystallinity and structural order after exfoliation. Note that, in several cases, small amounts of MX phases (with a rock-salt crystal structure) were present in the initial powders. These do not react and the full width at half-maximum, FWHM, of their peaks remains unchanged after HF treatment. In sharp contrast, the (0002) peaks of the treated powders are all shifted to lower angles corresponding to higher c parameters. The same peaks also broaden considerably. Using the Scherrer formula, the effects of HF treatment on the c lattice constant and the average domain size along [0001] deduced from the FWHM and the Scherrer formula are listed. The penultimate column shows the estimated process yields. The last column lists the figures associated with each compound.

<table>
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<tr>
<th>compound</th>
<th>HF conc. (%)</th>
<th>time (h)</th>
<th>before HF</th>
<th>after HF</th>
<th>domain size (nm)</th>
<th>yield (wt %)</th>
<th>associated figures</th>
</tr>
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<tr>
<td>Ti3AlC</td>
<td>10</td>
<td>10</td>
<td>1.36</td>
<td>1.504</td>
<td>6</td>
<td>60</td>
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<td>72</td>
<td>2.408</td>
<td>3.034</td>
<td>38</td>
<td>90</td>
<td>2B, 3B, 4D, 5D, 6A–D, and 8A</td>
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<tr>
<td>Ti3AlCN</td>
<td>50</td>
<td>18</td>
<td>1.841</td>
<td>2.051</td>
<td>11</td>
<td>100</td>
<td>4A, B</td>
</tr>
<tr>
<td>(V0.5,Cr0.5)3AlC2</td>
<td>50</td>
<td>28</td>
<td>1.379</td>
<td>1.488</td>
<td>5</td>
<td>80</td>
<td>2C, 3C, 4E, 5C and 7A,B</td>
</tr>
<tr>
<td>Ta4AlC3</td>
<td>50</td>
<td>72</td>
<td>1.841</td>
<td>2.051</td>
<td>11</td>
<td>100</td>
<td>4A, B</td>
</tr>
</tbody>
</table>

*The particle size for all MAX phases was <35 μm prior to exfoliation. The effects of HF treatment on the c lattice constant and the average domain size along [0001] deduced from the FWHM and the Scherrer formula are listed. The penultimate column shows the estimated process yields. The last column lists the figures associated with each compound.

Figure 2. Photograph of cold-pressed, free-standing discs with diameters of 25 mm of (A) Ti2C, (B) Ta2C3, (C) TiNbC, and (D) Ti3C2.

The SEM image of Ti3AlC2 after the HF treatment (Figure 4C) confirms successful exfoliation of individual particles, which is similar to what was reported for exfoliated graphite31–33 or Ti3AlC2 (Figure 4B)
2-D sheets, and energy-dispersive X-ray (EDX) microanalysis after exfoliation showed the Ti/C/F/O \( \approx \) atomic ratios to be 39:19:20:22, respectively. The absence of Al suggests the following reaction:

\[
\text{Ti}_2\text{AlC} + 3\text{HF} \rightarrow \text{Ti}_2\text{C} + \text{AlF}_3 + 3/2\text{H}_2
\]  

This reaction is presumably followed by reactions 3 and 4 and results in 2-D layers of Ti\(_2\)C with hydroxyl and/or F surface groups; the latter explains the presence of O and F after treatment. Note that whenever the MAX powders were immersed in the HF solution, bubbles, presumably H\(_2\), were observed.

\( \text{Ta}_4\text{AlC}_3 \). After HF treatment (50% HF for 72 h), the XRD (Figure 3B-c) and electron microscopy (Figure 4D) document the successful exfoliation of \( \text{Ta}_4\text{AlC}_3 \). We note that the (0002) XRD peak after treatment has a clearly visible shoulder. Peak deconvolution yields a first reflection ascribed to a \( c \) parameter of \( \approx 3.034 \) nm (domain size of \( \approx 38 \) nm; i.e., about 12 unit cells along [0001]) and a second peak corresponding to a \( c \) parameter of 2.843 nm (domain size of \( \approx 18 \) nm; i.e., about 6 unit cells along [0001]). The reason for the shoulder is unclear at this time, and one possible explanation is that the untreated powders contained two polymorphs of \( \text{Ta}_4\text{AlC}_3 \). This comment notwithstanding, more work is needed to understand the origin of the observed shoulder.

The TEM micrographs of HF treated \( \text{Ta}_4\text{AlC}_3 \) are shown in Figure 5D. Figure 6A shows a higher

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**Figure 3.** XRD patterns before and after HF treatment at room temperature for (A) \( \text{Ti}_2\text{AlC} \) (10% HF for 10 h), (B) \( \text{Ta}_4\text{AlC}_3 \) (50% HF, 72 h), (C) \( \text{TiNbAlC} \) (50% HF 28 h), and the inset is the XRD for \( (\text{V}_{0.5}\text{Cr}_{0.5})_3\text{AlC}_2 \) (50% HF 65 h) and cold-pressed zoomed-in on the (0002) peak, and (D) \( \text{Ti}_3\text{AlCN} \) (30% HF 18 h). The diffractograms of each panel represent, from bottom to top, (a) MAX phase before HF treatment, (b) MAX phase after HF treatment, (c) cold-pressed MXene after HF treatment of MAX phases, and (d) MAX phase cold-pressed prior to HF treatment.
Figure 4. Secondary electron SEM micrographs for (A) Ti$_3$AlC$_2$ particle before treatment, which is typical of unreacted MAX phases, (B) Ti$_3$AlC$_2$ after HF treatment, (C) Ti$_3$AlC after HF treatment, (D) Ta$_4$AlC$_3$ after HF treatment, (E) TiNbAlC after HF treatment, and (F) Ti$_3$AlCN after HF treatment. In (B–F), the exfoliation is obvious.

Figure 5. TEM images for (A) Ti$_3$C$_2$ layers formed after HF treatment of Ti$_3$AlC$_2$ at room temperature for 22 h assuming a single sheet (monolayer) is the most transparent part of the sample, (B) similar layers of Ti$_2$CN$_x$ exfoliated from Ti$_3$AlCN by HF treatment, (C) TiNbAlC after HF treatment, and (D) Ta$_4$AlC$_3$ after HF treatment. Numbers show an increasing number of layers from the thinnest and most transparent to electrons (1, presumably a monolayer) to 2, 3, or more layers.
magnification high-resolution transmission electron microscope (HRTEM) image of a Ta₄C₃ layer with some nanometer sized holes. Similar atomic defects were reported in functionalized graphene. The latter can act as nucleation sites for metal oxides which are useful in many applications. The electron energy loss spectra (EELS) (Figure 6B) confirm the presence of C, Ta, O (not shown), some F (not shown) and the absence of Al, confirming that it was etched out from the structure.

HRTEM and selected area electron diffraction (SAED) (Figure 6C,D), however, show that the crystallinity of the basal planes of the MAX phases is preserved. These images confirm the hexagonal structure of the Ta₄C₃ layers. Measurements of the d spacings shown in the figure resulted in 0.269 and 0.155 nm for the (0110) and (2110) lattice planes, respectively. When these values are used to calculate the a lattice parameter, the value obtained, 0.31 nm, is in excellent agreement with that of the a paraeter of the nonexfoliated Ta₄AlC₃ MAX phase, viz. 0.311 nm. It is thus reasonable to conclude that the MAX crystal structure of the basal planes is maintained in the MXenes.

As shown in Figure 8A, the Ta₄C₃ layers are not just electronically transparent but also optically transparent under an OM in transmittance mode. After exfoliation, EDX showed the Ta/C/F/O atomic ratios to be 40:39:7:14, respectively. The absence of Al, together with the other evidence, suggests the following reaction:

\[ \text{Ta}_{4}\text{AlC}_3 + 3\text{HF} = \text{Ta}_4\text{C}_3 + \text{AlF}_3 + 1.5\text{H}_2 \]  

This reaction is presumably followed by reactions 3 and 4.

**Figure 6.** Electron microscopy analysis of Ta₄AlC₃ after HF treatment (A) TEM image, (B) EELS and inset showing a low-magnification TEM image, (C) HRTEM of multilayer MXene, and (D) SAED.

The XRD patterns for TiNbAlC, before and after HF treatment (Figure 3C), show that the intensity of the TiNbAlC peaks decreased significantly after HF treatment (considering that 10 wt % Si was used as an internal reference) and a new broad peak at ≈11.8° 2θ appeared after cold pressing (Figure 3C-c), similar to what was reported previously. Here again a shoulder at a larger d spacing compared to the main peak is observed. The latter is most likely due to some exfoliated (Ti₀.₅,Nb₀.₅)₃AlC₂ that was present as a second phase in the starting powder, similar to what was discussed above and shown in Figure 3A-c.

SEM micrographs (Figure 4E) clearly show exfoliated TiNbAlC particles. TEM micrographs, after sonication (Figure 5C), show thin sheets composed of Ti, Nb, C, O, and F in an atomic ratio that EDX shows to be 14:16:23:34:13, respectively. TEM micrographs (Figure 5C) are noteworthy in that the carbon grid is visible through TiNbC layers. Given the fact that Ti and Nb are heavy elements, this implies that the layers must be quite thin indeed.

HRTEM of a TiNbC layer, shown in Figure 7A, and its corresponding SAED (inset) again show hexagonal symmetry. At 0.2606 nm, the perpendicular separation of the (10̅10) lattice planes results in an a lattice constant of 0.301 nm, a value that is in good agreement with what was reported for TiNbAlC, viz. 0.308 nm. Figure 7B shows EELS for TiNbAlC after HF treatment and confirms the presence of Ti, Nb, C, F (not shown), and O, but no Al.

As noted above, the (V₀.₅,Cr₀.₅)₃AlC₂ powders did not undergo complete exfoliation as indicated by the presence of two distinct peaks in the inset of Figure 3C.
All other observations are consistent in that at least a fraction was exfoliated. Note that by varying the concentration and/or reaction times, fully exfoliated \((V_{0.5},Cr_{0.5})_3C_2\) 2-D layers should be readily obtainable. HRTEM for an exfoliated layer of \((V_{0.5},Cr_{0.5})_3C_2\) after HF treatment (Figure 7C) and its corresponding SAED (inset) confirm the same hexagonal crystal structure as was shown for all previous exfoliated phases. At 0.286 nm, the \(a\) lattice parameter, calculated from the (01T0) reflections, is in excellent agreement with that of \((V_{0.5},Cr_{0.5})_3AI_2C_2\), viz. 0.289 nm. Figure 7D shows EELS for \((V_{0.5},Cr_{0.5})_3AI_2C_2\) after HF treatment and confirms the presence of \(V\), \(Cr\), \(C\), \(F\) (not shown), and \(O\) but no \(Al\).

**Ti\(_3\)AlCN.** HF treatment (30% HF, 18 h) of the Ti\(_3\)AlCN powders resulted in complete exfoliation as evidenced
The densities were estimated from the dimensions and weights of the cold-pressed discs. Number in parentheses is relative theoretical density assuming OH termination of MXene surfaces and the c parameter listed in Table 1.

A picture of the cold-pressed discs of the different MXene compositions is shown in Figure 2. Their densities (Table 2) varied between 2.91 g/cm³ for Ti₂C to 6.82 g/cm³ for Ta₄C₃. If one assumes the c lattice parameter listed in Table 1 and OH terminated surfaces of MXene sheets, then it is possible to calculate the theoretical densities. The last row in Table 2 lists the measured densities of the pressed discs. The numbers in parentheses list the % of theoretical densities that ranged from 50 to ~65%.

The sheet resistivity and resistivities of the various MXene discs are also shown in Table 2. Generally, these values are comparable to multilayer graphene reported by Li et al. and Blake et al. The resistivity values are higher than the MAX phases before treatment (<10 Ohm·m) presumably because of the replacement of the A layers with OH and/or F. When it is assumed that surface groups are similar in all of the exfoliated MAX phases, the difference in the resistivity between the different phases can be partially explained by the different number of atomic layers (3, 5, and 7 for MₓX, MₓX₂, and MₓX₃ phases, respectively). It is important to note that the resistivity values reported in Table 2 should be significantly higher than single MXene sheets because of the method by which the resistivity was measured. For example, the resistivity of bulk sintered Ti₃AlC₂ is 0.39 μΩ·m. When Ti₃AlC₂ powders were cold-pressed at 1 GPa, their resistivity increased to 1200 μΩ·m, a roughly, 3000 time increase.

Contact angle measurement results for water droplets on the cold-pressed discs of exfoliated phases are also listed in Table 2. These values are lower than those of the corresponding MAX phases—that were also measured in this work on cold-pressed samples, which were around 60°. The reduction in contact angle can be explained by the presence of OH surface groups after the HF treatment. In contradistinction, graphene can be transformed from superhydrophobic to superhydrophilic by altering the surface groups. The hydrophilicity of the MXenes would be an advantage when using aqueous electrolytes in energy storage devices or dispersing in water and alcohols for further processing.

Lastly, it is important to note that the only other transition metal elements that form MAX phases not included above are Hf, Mo, and Zr. These elements do not form MAX phases with Al, the focus of this study. On the basis of our work, however, we believe that it is only a matter of time before 2-D Hf₂C, Mo₂C, and Zr₂C are also synthesized. The same applies to the following nitride phases: Ti₄N₃, Ti₂N, Cr₂N, Zr₂N, and Hf₂N although at this time the stability of N-containing MXenes is lower than their carbide counterparts. In short, we are looking at a large number of 2-D early transition metal carbides, nitrides, and/or carbonitrides. The latter is especially true when solid solutions on the M and X sites, or both, are factored in.

In particular, tailoring surface functional groups of MXene 2-D layers presents itself as another variable for tuning their surface (e.g., wetting) and electrical (e.g., band gap, conductivity) and electrochemical (e.g., pseudocapacitance) properties, like in graphene. With such a large variety of possible chemistries, it is reasonable to assume that at least some of them will have unique enough properties to lead to applications in multiple fields and technologies, such as catalysis, energy storage/pseudocapacitors, and Li-ion batteries as we have just shown for Ti₂C, as well as potential reinforcements in polymers. The resulting 2-D layers are stiff when pulled parallel to the basal planes, quite conductive (Table 2), and should be more oxidation resistant than graphene because the oxide/hydroxide layer present on their surfaces may offer protection.

**CONCLUSIONS**

Recently, we showed that when Ti₃AlC₂ powders were immersed in HF, the Al layers were selectively extracted to yield 2-D Ti₃C₂ layers terminated with OH and/F surface groups. Herein we significantly expand this nascent large family of 2-D, Mₓ−1Xₙ layers to Ti₂C,
that were produced by cold pressing the powders at loads as-fabricated and HF-treated powders deposited on glass slides in all cases, we not only compared the diameter and given that both MAX and MXenes are easily oriented, broadening.

calibrate the diffraction angles and the instrumental peak described above.

using Cu Kα obtained with a powder diffractometer (Siemens D500, Germany) several times using deionized water and centrifuged to separate summarized the times and concentrations used. Table 1 Lawn, NJ) solutions of varying potency for various times. Table 1 powders were produced by milling as above. After cooling to room temperature, powder was produced by milling in a tube furnace to 1500 °C/C176 for 1 h under flowing Ar, and heated at 10 °C/min to 1500 °C for 1 h. The resulting dense discs were then milled using a titanium-nitride-coated milling bit to obtain powders for further study. In all cases, the milled powder was sieved through a ~400 mesh screen such that the initial particle size was <35 μm.

The TiNbAlC powders were made by mixing elemental tantalum, Ta (Alfa Aesar, Ward Hill, USA, 99.5 wt % purity; −325 mesh), niobium, Nb (Atlantic Equipment Engineers, Bergenfield, USA, 99.8 wt % purity; −325 mesh), and the same Al and C used above, in the molar ratio of 1:1:1:2, respectively, in a ball mill for 12 h. The powders were then heated at the rate of 10 °C/min in a tube furnace to 1500 °C for 1 h under flowing Ar. After cooling to room temperature, powders were processed as described above.

The (V0.5,Cr0.5)3AlC2 powders were made by mixing elemental tantalum, Ta (Alfa Aesar, Ward Hill, USA, 99.97 wt % purity; particle size <10 μm), tantalum, Ta (Alfa Aesar, Ward Hill, USA, 99.5 wt % purity; −325 mesh), chromium, Cr (Alfa Aesar, Ward Hill, USA, 99 wt % purity; −325 mesh), and the same Al and C used above, in the molar ratio of 1.5:1.3:1:2.2, respectively, in a ball mill for 12 h.

The mixed powders were then heated 10 °C/min to 1500 °C and held at that temperature in a tube furnace under flowing Ar for 2 h. After cooling to room temperature, powders were produced by milling as above.

The TiAlCN powders were made by mixing elemental Ti (Alfa Aesar, Ward Hill, USA, 99.5 wt % purity; −325 mesh), niobium, Nb (Atlantic Equipment Engineers, Bergenfield, USA, 99.8 wt % purity; −325 mesh), and held at that temperature in a tube furnace under flowing Ar for 2 h. After cooling to room temperature, powders were produced by milling as above.

Each of the aforementioned MAX phase sieved powders was immersed at room temperature in HF (Fisher Scientific, Fair Lawn, NJ) solutions of varying potency for various times. Table 1 summarizes the times and concentrations used. In all cases, the resulting suspension was then washed several times using deionized water and centrifuged to separate the powders from the supernatant.

Characterization. X-ray diffraction (XRD) patterns were obtained with a powder diffractometer (Siemens D500, Germany) using Cu Kα radiation and a step scan of 0.02° and 1 s per step. Si powder was added to some samples as an internal standard to calibrate the diffraction angles and the instrumental peak broadening.

To accentuate that HF treatment mostly affects the c parameter and given that both MAX and MXenes are easily oriented, in all cases, we not only compared the diffractograms of the as-fabricated and HF-treated powders deposited on glass slides but more importantly we also compared diffractograms of discs that were produced by cold pressing the powders at loads corresponding to 1 GPa. In all cases, the cold pressing resulted in thin, free-standing discs shown in Figure 2.

A scanning electron microscope, SEM (Zeiss Supra 50VP, Germany), was used to obtain high-magnification images of the treated powders and conduct elemental analysis via energy-dispersive X-ray (EDX) spectroscopy. After sonication, the 2-D sheets were investigated by transmission electron microscopy, TEM (JEOL JEM-2100, Japan), with an accelerating voltage of 200 kV. Electron energy loss spectroscopies (EELS) were obtained using FEI Tecnai G2 TF 20 UT field emission gun TEM operated at 200 kV with 0.19 nm point resolution and 0.7 eV energy resolution for EELS. The TEM samples were prepared by suspending the powders in isopropanol alcohol and placing a drop of the latter on a lacey carbon coated 200 mesh Cu grid.

After HF treatment and sonication of the resultant powder in isopropanol alcohol, a droplet from the suspension was placed on a glass slide and investigated using an optical microscope, OM (SBAP0: Leica Microsystems Inc., Bannockburn, IL, USA) in transmitted light mode.

to measure the sheet resistances and the contact angle, MXene discs (25 mm in diameter, 300 μm thick) were cold-pressed from the reacted powders. The latter were placed in a die and cold-pressed to a load corresponding to a stress of 1 GPa (Figure 2).

The surface or sheet resistances of cold-pressed, free-standing MXene discs (Figure 2) were measured using a four-probe technique (Cascade Probe Station CPS-1303-24 with 4-point probe head Alesi CAS-57, Cascade Microtech, Inc., Beaverton, USA).

Contact angle measurements of deionized water were also performed at room temperature using the sessile drop technique. Ten microliter water drops were placed on the surfaces of cold-pressed MXene discs. The contact angles were measured from photographs taken with a CCD camera yielding an accuracy of approximately ±3°.

Conflict of Interest: The authors declare no competing financial interest.

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REFERENCES AND NOTES


