Termination-Property Coupling via Reversible Oxygen Functionalization of MXenes

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ABSTRACT: MXenes are a growing family of 2D transition-metal carbides and nitrides, which display excellent performance in myriad of applications. Theoretical calculations suggest that manipulation of the MXene surface termination (such as ==O or −F) could strongly alter their functional properties; however, experimental control of the MXene surface termination is still in the developmental stage. Here, we demonstrate that annealing MXenes in an Ar + O₂ low-power plasma results in increased ==O functionalization with minimal formation of secondary phases. We apply this method to two MXenes, Ti₃CT₄ and Mo₂TiC₂Tₓ (Tₓ represents the mixed surface termination), and show that in both cases, the increased ==O content increases the electrical resistance and decreases the surface transition-metal's electron count. For Mo₂TiC₂Oₓ, we show that the O content can be reversibly altered through successive vacuum and plasma annealing. This work provides an effective way to tune MXene surface functionalization, which may unlock exciting surface-dependent properties.

KEYWORDS: MXenes, 2D materials, surface functionalization, electron energy loss spectroscopy, oxidation state analysis, electrical resistance measurements

MXenes are a quickly expanding family of 2D materials that show exceptional promise for applications ranging from electromagnetic interference shielding to energy storage, gas sensing, flexible electronics, and medicine.¹⁻⁴ The MXene general formula is Mₓ+nXₙ where M represents one or more transition-metal element(s), X is C and/or N, and n = 1−4. So far, over 30 stoichiometric MXenes have been experimentally synthesized. In contrast to other 2D materials such as graphene or transition-metal dichalcogenides, bare MXene surfaces are composed of transition-metal layers, which are reactive and readily form chemical bonds with available terminating moieties. In fact, the MXene surfaces are invariably functionalized during synthesis, usually with a non-uniform mixture of −OH, −F, −Cl, and −==O.⁵−¹² Thus, the MXene chemical formula is usually expanded to Mₓ+n¹XₙTₓ where T represents the mixed surface termination.

Tuning MXene functional properties via surface termination holds great promise, though this goal has yet to be fully experimentally realized. Numerous density functional theory (DFT) calculations have predicted that termination can strongly influence MXene properties such as Li ion capacity and mechanical strength, and in certain MXenes, altering the termination is predicted to drive metal-to-insulator transitions (MITs).⁶,¹³−¹⁶ However, the metastable nature of MXenes and the relatively strong M−T bonds make it difficult to alter the as-synthesized mixed surface termination without degrading the underlying MXene structure. One approach to solve this problem is the development of novel synthesis methods.¹⁷−²¹ Notably, the use of molten salt reactions shows great promise for the precise control of a wide range of surface groups.²²,²³ A second route is post-synthesis treatment, such as vacuum annealing or controlled exposure to chemical reagents.²⁶,²⁷ For example, Persson et al. recently reported on the annealing of individual Ti₃C₂Tₓ flakes in a low-pressure O₂ environment and obtained full ==O functionalization,²⁶ though TiO₂ was formed as a secondary phase.²⁶,²⁷ Despite these successes, methods to reliably and reversibly alter the MXene termination require further development. Moreover, there are only a few available reports which correlate the MXene surface termination with physical and chemical properties.

Here, we report a plasma annealing method for ==O surface functionalization, which shows promise for reversible termination control in MXene thin films, with minimal secondary oxide formation (Figure 1a). Specifically, we iteratively performed vacuum annealing to drive surface defunctionalization, followed by Ar + O₂ plasma annealing to refuctionalize
MXene structure, chemistry, and electronic properties were monitored in situ using electron diffraction, electron spectroscopy, and resistance versus temperature (R vs T) measurements, respectively. We apply this technique to two MXenes, Mo$_2$TiC$_2$T$_x$ and Ti$_2$CT$_x$ (Figure 1b,c), both of which show metallic conductivity in their as-synthesized, mixed-termination state but are predicted to undergo a MIT upon complete =O functionalization. For both MXenes, our plasma annealing method leads to increased =O termination, a concomitant decrease in the surface metal’s d orbital occupancy, and an increase in the electrical resistance. However, neither MXene displayed an =O induced MIT, which motivates further theoretical efforts. For Mo$_2$TiC$_2$T$_x$, we show that =O can be reversibly added and removed from the MXene surface, and we demonstrate uniform =O functionalization. Conversely, for Ti$_2$CT$_x$, reversible control of =O termination was not achieved, reflecting the differences in strength, thermal stability, and M–T bond energy between these two MXenes.

Details of the bulk Mo$_2$TiAlC$_2$ and Ti$_2$AlC MAX phase synthesis are given in the Supporting Information. From the parent MAX phases, aqueous solutions of single-flake MXenes were synthesized according to ref 31; further details are given in the Supporting Information. Scanning electron microscopy images of individual Mo$_2$TiC$_2$T$_x$ and Ti$_2$CT$_x$ MXene flakes are shown in Figure 1d,e, respectively. To enable our annealing experiments, we spin-coated MXene films onto transmission electron microscope (TEM) chips that allow in situ annealing and imaging within TEM (Supporting Information, Figure 1). The spin-coated MXene films were spatially uniform, consisting of many restacked, overlapping c-axis-oriented flakes, with thicknesses in the range of 10–50 nm. This structure is evidenced in the high-resolution TEM (HRTEM) image, as shown in Figure 1f. No individual atomic columns are observed, but clear rings are revealed in the image Fourier transform, indicative of many overlapping c-axis-oriented flakes with random in-plane rotations. The electron diffraction pattern in Figure 1g confirms this interpretation, showing strong rings corresponding to the MXene (101) and (110) reflections, as expected for our sample geometry. Given the synthesis treatments used here, the as-deposited Ti$_2$CT$_x$ has initial =O, =OH, and =F termination and Li$^+$ and H$_2$O intercalation, and no secondary phases or contaminants are observed. The as-deposited Mo$_2$TiC$_2$T$_x$ has =O and =OH termination and H$_2$O and tetramethylammonium cation (TMA$^+$) intercalation. There are also trace amounts (≤1 at %) of calcium oxide contaminants in our Mo$_2$TiC$_2$T$_x$ samples, as determined from electron energy loss spectroscopy (EELS) elemental analysis and electron diffraction (Supporting Information, Figure 2). We note here that multiple Ti$_2$CT$_x$ and Mo$_2$TiC$_2$T$_x$ samples were tested and showed qualitatively similar behavior (see Supporting Information, Figures 3–6).

Our experimental approach is schematically outlined in Figure 1a. With the end goal of obtaining homogeneous =O functionalization, it is first necessary to remove intercalation species and other termination moieties. Because =O termination is more stable than =OH or =F, vacuum annealing can be used to (partially) remove the non =O termination and intercalants. To this end, samples were initially annealed at high temperature (400–800 °C) under the vacuum of TEM (∼10$^{-7}$ torr). Then, to (re)functionalize the exposed M-sites with =O, we removed the sample holder from the transmission electron microscope and inserted it into a plasma chamber. Samples were annealed from 100–300 °C in an Ar + O$_2$ plasma (80% Ar and 20% O$_2$) at ∼1 mbar and 18 W. During sample transfer to and from the plasma chamber, the samples were exposed to the ambient atmosphere for ∼10 s; however, we find that this brief exposure does not alter the oxygen content of our MXene films (Supporting Information, Figure 7). After each annealing step, EELS and electron diffraction patterns were collected from the same location of each sample to determine the composition and structure. EELS and diffraction data collected after in situ TEM vacuum annealing are labeled as V_temp, where “temp” is the vacuum temperature.
annealing temperature in °C, and these measurements are shown with blue curves. Measurements after Ar + O₂ plasma treatments are labeled as O_temp and are shown with red curves. We used heating and cooling rates of 1 °C/s. For vacuum annealing steps, the maximum temperature was held for 5 min, and for plasma annealing steps, the maximum temperature was held for 1 min.

Our ability to alter the surface termination in Mo₂TiC₂Tₓ is summarized in Figure 2a–c. For this sample, we used the following annealing sequence: V₂₃₀ → V₆₀₀ → O₁₅₀ → O₂₅₀ → V₆₀₀₂nd. Figure 2a shows the EELS O K-edge measured after each annealing step, and the changes in edge height are directly proportional to changes in the oxygen concentration. Figure 2b quantifies the EELS data and plots changes in the termination concentration. Lastly, Figure 2c shows the electron diffraction data. Owing to the rotational symmetry of the diffraction patterns (Figure 1g), we perform a rotational average on the raw 2D diffraction data and present the rotationally averaged electron diffraction (RAED) data, as intensity versus momentum transfer (Q). The initial 300 °C annealing step was used to drive H₂O deintercalation, which could otherwise complicate O K-edge EELS analysis and O concentration determination. The following 600 °C vacuum anneal, aimed at removing −OH and ←O termination, resulted in a significant decrease in the O K-edge intensity. Presumably, the measured decrease in the O K-edge intensity has contributions from the loss of both −OH and ←O species; however, we cannot differentiate these two moieties with EELS. Regardless, after the 600 °C annealing step, we conclude that only ←O remains since −OH desorbs at temperatures well below 600 °C.²⁵ Following the 600 °C vacuum anneal, plasma annealing at 150 °C led to a substantial increase in the ←O concentration, and subsequent plasma annealing at 250 °C produced fully functionalized Mo₂TiC₂O₂₁ (for all given MXene composition Mₓ₁XₓTₓ, the error in x is ±0.1). To demonstrate the reversibility of this process, we then performed a second vacuum annealing step at 600 °C, which reduced the ←O concentration to Mo₂TiC₂O₁₇. Note that the RAED data show no emergence of secondary phases throughout the entire experiment (Figure 2c), confirming the integrity of the MXene structure. We also note that while the O K-edge intensity changed substantially (which reflects changes in the oxygen content), changes to the fine structure of the O K-edge were negligible (Figure 2a and Supporting Information, Figure 8). The O K-edge fine structure reflects the bonding environment of oxygen; thus, the constant fine structure indicates that oxygen was added (and removed) from the sample in the form of ←O termination, as opposed to incorporation into secondary oxides. Similarly, the C K- and Ti L-edges show negligible fine structure changes with annealing, further verifying retention of the MXene structure throughout all the annealing steps (Supporting Information, Figure 9). These data represent reversible surface termination control in Mo₂TiC₂Oₓ-

For Ti₂CTₓ, the goal of obtaining uniform ←O termination is impeded by three factors: initial −F termination which must be removed, lower thermal stability of Ti₂CTₓ compared to Mo₂TiC₂Tₓ, and stronger Ti–T bonding relative to Mo–T bonding.¹⁰,²²,²⁰ Consequently, attempts to completely remove −F with high-temperature vacuum annealing consistently failed; secondary oxides formed prior to complete −F removal. Thus, with the aim of minimizing −F while avoiding secondary phase formation, we used the following annealing sequence: V₂₀₀ → V₄₅₀ → O₁₅₀ → O₂₀₀. The EELS and RAED data are shown in Figure 2d–f. The initial 200 °C vacuum anneal was intended to remove H₂O intercalation, and the following 450 °C vacuum anneal resulted in a slight reduction in the −F concentration. Subsequent plasma annealing at 150

Figure 2. (a) O K-edge of Mo₂TiC₂Tₓ after various annealing steps. The edge intensity was normalized based on the Ti L-edge intensity, see Supporting Information Figure 3. (b) Termination composition of the same Mo₂TiC₂Tₓ sample, as determined from the EELS data. (c) RAED of Mo₂TiC₂Tₓ after various annealing treatments. The legend in (a) applies to (c) as well. (d–f) Same as (a–c) but for a Ti₂CTₓ sample. In (f), * marks anatase Ti oxide peaks. The 2D electron diffraction patterns used and the generated RAED profiles are given in Supporting Information (Figure 10).
°C increased the \( =\text{O} \) content, giving a composition of \( \text{Ti}_2\text{C}_3\text{O}_x\text{F}_{0.3} \) with fully saturated Ti surface sites. We note that for these annealing steps (\( V_200, V_450, \) and \( O_{150} \)), the RAED shows no evidence of secondary phase formation, and the \( \text{O} \ K\)-edge only changes in magnitude, with the fine structure remaining constant. These findings indicate that only the surface termination concentration is altered, while the underlying Ti\(_3\)C structure remains intact. An additional plasma anneal at 200 °C further increased the \( \text{O} \) content, resulting in a composition of \( \text{Ti}_2\text{C}_3\text{O}_x\text{F}_{0.3} \) and suggesting super saturation of the MXene surface.\(^{36}\) However, a broad peak in the RAED data at \( Q \sim 3 \text{ nm}^{-1} \) suggests some degree of MXene degradation during the \( O_{200} \) anneal, and the excess \( \text{O} \) could be contained within amorphous secondary phases. Final anneal at 200 °C did not result in any \( =\text{O} \) loss, but a measurable fraction of TiO\(_2\) was observed, as evidenced by the TiO\(_2\) peaks seen in the RAED data (Figure 2f). In contrast to \( \text{Mo}_2\text{TiC}_3\text{T}_x \), the inability to reversibly control \( =\text{O} \) in \( \text{Ti}_3\text{CT}_x \) reflects the known differences in thermal stability and \( \text{M} \rightarrow \text{T} \) bond strength of these two MXenes.\(^{10,22,30}\)

Having altered the \( =\text{O} \) concentration in both \( \text{Mo}_2\text{TiC}_3\text{T}_x \) and \( \text{Ti}_3\text{CT}_x \), we next consider how changes in \( \text{T} \) influence the surface \( \text{M-site} \) chemistry. This is a critical question for understanding termination-property coupling as oxidation state changes in transition metal compounds are often associated with changes in magnetism, MITs, and other functional properties.\(^{33}\) For our \( \text{Mo L-edge} \) EELS analysis of \( \text{Mo}_2\text{TiC}_3\text{T}_x \), we investigated a separate sample than that shown in Figure 2. The \( \text{Mo}_2\text{TiC}_3\text{T}_x \) sample investigated with \( \text{Mo L-edge} \) EELS (as shown in Figure 3a) had an annealing sequence of \( V_200 \rightarrow V_700 \), and the measured post-anneal compositions were \( \text{Mo}_2\text{TiC}_3\text{O}_{1.1} \rightarrow \text{Mo}_2\text{TiC}_3\text{O}_{1.3} \) (Supporting Information, Figure 3). With vacuum annealing and decreased \( =\text{O} \) concentration, the measured \( \text{Mo L}_{\text{3,2}} \) and \( \text{L}_{\text{2,3}} \) edge intensities decreased substantially. Within the experimental energy resolution and signal-to-noise ratio, no discernible changes in the \( \text{Mo L}_{\text{3,2}} \) edge shapes were observed. For \( \text{Ti L-edge} \) spectra and their evolution with annealing, the \( \text{Ti L}-\text{edges} \) (Figure 3b) show no evidence of secondary phase formation, and the \( \text{O} \) concentration in both \( \text{Mo}_2\text{TiC}_3\text{T}_x \) and \( \text{Ti}_3\text{CT}_x \) increased significantly with each annealing step. The \( \text{O} \) content and intensities were normalized to the post-670 eV, and the \( \text{Mo L-edge} \) data were normalized to the post-L-3-edge intensity, from 2560 to 2640 eV.

**Figure 3.** (a) \( \text{Mo L}\text{-edges of Mo}_2\text{TiC}_3\text{T}_x \) after vacuum annealing. (b) \( \text{Ti L}\text{-edges of Ti}_3\text{CT}_x \) after various annealing steps. Due to the energy drift of the TEM, all edges were aligned to their edge onset. All spectra were deconvolved to remove plural scattering. The \( \text{Ti L-edges} \) were normalized to the post-edge continuum intensity (at 472 eV), and the \( \text{Mo L-edge} \) data were normalized to the post-L-3-edge intensity.

**Table 1. Comparison of EELS Fine Structure Analysis for Mo\(_2\text{TiC}_3\text{T}_x \) and Ti\(_3\text{CT}_x \) MXenes\(^{43,44}\)**

| \( \text{Mo}_2\text{TiC}_3\text{T}_x \) | \( \text{Ti}_3\text{CT}_x \) |
|---|---|
| \( V_200 \) | \( V_700 \) | \( V_200 \) | \( V_450 \) | \( O_{150} \) | \( O_{200} \) |
| \( \text{O}_x \) | 2.1 | 1.5 | 1.5 | 1.5 | 1.8 | 2.0 |
| \( L_3 + L_2 \) | 1.00 | 0.85 | 1.00 | 1.01 | 1.11 | 1.19 |
| \( L_3/L_2 \) | 0.54 | 0.54 | 0.43 | 0.43 | 0.44 | 0.44 |

\(^{43} \text{The O}_x \text{ row indicates the value of } x \text{ in } \text{Mo}_2\text{TiC}_3\text{O}_x \text{ and } \text{Ti}_3\text{CF}_x\text{O}_x \text{.} \)

\(^{44} \text{For the } L_3 + L_2 \text{ row, the values were normalized to the initial measurement.} \)

\(^{45} \text{The * marking the } \text{Ti}_3\text{CT}_x \text{ O}_{200} \text{ column indicates that some MXene degradation and oxide formation may be present.} \)

however, differences in the \( L_3/L_2 \) intensity ratio were within the analysis uncertainty and showed no strong trend (Table 1).

Lastly, we consider how changes in the \( =\text{O} \) content and \( d \) orbital occupancy correlate with the electronic transport properties of \( \text{Ti}_3\text{CT}_x \) and \( \text{Mo}_2\text{TiC}_3\text{T}_x \). After each annealing step, we measured the resistance of the sample as a function of temperature (\( R \) vs \( T \)) upon cooling from 200 °C (Figure 4a,b). Note that the \( \text{Mo}_2\text{TiC}_3\text{T}_x \text{ R vs } T \) data presented here comes from the same sample as described in Figure 2. To understand changes in \( R \) vs \( T \) in the context of surface chemistry, we plot the room-temperature resistance (\( R_{\text{RT}} \)), the temperature dependence of resistance (\( \text{dR}/\text{dT} \)) at room temperature, and the \( =\text{O} \) termination content as a function of annealing conditions (Figure 4c.d). Somewhat surprisingly, \( \text{Ti}_3\text{CT}_x \) and \( \text{Mo}_2\text{TiC}_3\text{T}_x \) displayed metallic conductivity (positive \( \text{dR}/\text{dT} \)).
for all annealing conditions; we did not observe a MIT in either $\text{TiC}_2\text{O}_3\text{F}_{0.3}$ or $\text{MoTiC}_2\text{O}_{2.1}$. For $\text{TiC}_2\text{T}_x$, the absence of a MIT with increased $\equiv\text{O}$ functionalization may be due to the residual $\equiv\text{F}$ content since $\text{Ti}_2\text{CF}_2$ is predicted to be a metal.\textsuperscript{40} Importantly, $\text{TiC}_2\text{O}_{1.0}\text{F}_{0.3}$ showed an almost temperature-independent resistance in the entire range under study. This behavior is very important for electronic applications as it provides stable performance even upon large temperature fluctuations. For $\text{MoTiC}_2\text{O}_{2.1}$, the absence of semiconducting behavior may be related to extrinsic effects, for example, point defects or disorder of the Ti and Mo sublattices. Alternatively, the measured metallic conductivity may be an intrinsic property of $\text{Mo}_{2}\text{TiC}_2\text{O}_2$, as predicted in certain DFT studies.\textsuperscript{37,38}

Despite the absence of a MIT, interesting trends still emerge from the data presented in Figure 4. For both $\text{Mo}_{2}\text{TiC}_2\text{T}_x$ and $\text{TiC}_2\text{T}_x$, there is a clear correlation between $\equiv\text{O}$ content and $R_{\text{RT}}$. In a previous study, we found a similar correlation between $\equiv\text{F}$ content and $R_{\text{RT}}$ in $\text{Ti}_2\text{C}T_x$ and $\text{Ti}_2\text{CNT}_{2.2}$. For $\text{TiC}_2\text{T}_x$ and $\text{Ti}_2\text{CNT}_{2.2}$, an increased $\equiv\text{F}$ content also led to an increase in $dR/dT$. Conversely, in the present study, the increasing $\equiv\text{O}$ content caused a decrease in $dR/dT$ for $\text{TiC}_2\text{T}_x$, suggesting a different mechanism linking the surface termination and electrical resistance. However, we note the challenges associated with analysis of multi-flake MXene $R$ vs $T$ measurements, which include contributions from both inter-flake and intra-flake effects.\textsuperscript{22,39}

In conclusion, we used a low power Ar $+$ O$_2$ plasma annealing method to tune the $\equiv\text{O}$ functionalization in both $\text{Mo}_{2}\text{TiC}_2\text{T}_x$ and $\text{TiC}_2\text{T}_x$ films. For $\text{Mo}_{2}\text{TiC}_2\text{T}_x$, we obtained pure $\equiv\text{O}$ functionalization and were able to reversibly add and remove $\equiv\text{O}$ from the MXene surface. For both MXenes, increased $\equiv\text{O}$ functionalization leads to a decrease in the surface M-site $d$ orbital occupancy. This finding offers important insights into how surface termination alters the MXene chemistry with direct relevance for applications such as catalysis. From $R$ vs $T$ measurements, we found that increasing $\equiv\text{O}$ termination increased the MXene electrical resistance. Despite predicted MITs in both MXenes, we found that $\text{Mo}_{2}\text{TiC}_2\text{O}_{2.1}$ and $\text{TiC}_2\text{O}_{2.0}\text{F}_{0.3}$ are metallic, which motivates further theoretical investigation into the electronic structures of these materials. Notably, $\text{TiC}_2\text{T}_x$ approached temperature-independent resistance when the $\equiv\text{O}$ termination was maximized, which is important for certain electronic applications. At present, the microscopic mechanism of MXene functionalization during plasma annealing is not known, and additional work is needed in this direction. The plasma annealing method described here holds promise for control of MXene surface functionalization, which, in turn, allows tailoring of the MXene resistance and chemistry for application-specific property optimization.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnanoscienceau.2c00024.

Materials and methods; additional EELS and diffraction results; and data on additional $\text{TiC}_2\text{T}_x$ and $\text{Mo}_{2}\text{TiC}_2\text{T}_x$ samples (PDF)

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Figure 4. (a,b) $R$ vs $T$ results for $\text{Mo}_{2}\text{TiC}_2\text{T}_x$ and $\text{TiC}_2\text{T}_x$, respectively. (c,d) Analysis of the $R$ vs $T$ data for $\text{Mo}_{2}\text{TiC}_2\text{T}_x$ and $\text{TiC}_2\text{T}_x$, respectively. Lines are a guide for the eye.
Complete contact information is available at: https://pubs.acs.org/10.1021/acsnanoscienceau.2c00024

Author Contributions
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Notes
The authors declare no competing financial interest.

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