On the organization and thermal behavior of functional groups on Ti$_3$C$_2$ MXene surfaces in vacuum

To cite this article: Ingemar Persson et al 2018 2D Mater. 5 015002

View the article online for updates and enhancements.

Related content
- Layered ternary Mn$_x$LA$x$ phases and their 2D derivative MXene: an overview from a thin-film perspective
  Per Eklund, Johanna Rosen and Per O Å Persson

- Effect of surface functionalization on the electronic transport properties of Ti$_3$C$_2$ MXene
  G. R. Berdiyorov

- Ambient pressure photoelectron spectroscopy: Practical considerations and experimental frontiers
  Lena Trotechau, Ashley R Head, Osman Karslolu et al.
On the organization and thermal behavior of functional groups on Ti\textsubscript{3}C\textsubscript{2} MXene surfaces in vacuum

Ingemar Persson\textsuperscript{1}, Lars-Åke Näslund\textsuperscript{1}, Joseph Halim\textsuperscript{1,2}, Michel W Barsoum\textsuperscript{1,2}, Vanya Darakchieva\textsuperscript{1}, Justinas Palisaitis\textsuperscript{1}, Johanna Rosen\textsuperscript{1} and Per O Å Persson

\textsuperscript{1} Department of Physics Chemistry and Biology, Thin Film Physics Division, Linköpings Universitet, SE-581 83 Linköping, Sweden
\textsuperscript{2} Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, United States of America
\textsuperscript{3} Department of Physics Chemistry and Biology, Semiconductor Materials Division, Linköpings Universitet, SE-581 83 Linköping, Sweden

E-mail: ingemar.persson@liu.se

Keywords: MXene, Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, \textit{in situ} heating, STEM, temperature-programmed XPS, surface functionalization

Abstract

The two-dimensional (2D) MXene Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} is functionalized by surface groups (T\textsubscript{x}) that determine its surface properties for, e.g. electrochemical applications. The coordination and thermal properties of these surface groups has, to date, not been investigated at the atomic level, despite strong variations in the MXene properties that are predicted from different coordinations and from the identity of the functional groups. To alleviate this deficiency, and to characterize the functionalized surfaces of single MXene sheets, the present investigation combines atomically resolved \textit{in situ} heating in a scanning transmission electron microscope (STEM) and STEM simulations with temperature-programmed x-ray photoelectron spectroscopy (TP-XPS) in the room temperature to 750 °C range. Using these techniques, we follow the surface group coordination at the atomic level. It is concluded that the F and O atoms compete for the DFT-predicted thermodynamically preferred site and that at room temperature that site is mostly occupied by F. At higher temperatures, F desorbs and is replaced by O. Depending on the O/F ratio, the surface bare MXene is exposed as F desorbs, which enables a route for tailored surface functionalization.

Introduction

Since the discovery of graphene [1], two-dimensional (2D) materials have attracted vast attention as a consequence of their exceptional properties that arise from their reduced dimensionality as compared to their parent bulk materials. A few years ago, a new family of 2D transition metal carbides, MXenes, was discovered [2–4]. MXenes have been described as 2D-conductive clays [5] synthesized by exfoliation of the MAX phases, which are nanolaminated phases of carbides and/or nitrides following the general formula M\textsubscript{n–1}AX\textsubscript{n} (n = 1, 2 or 3), where M is an early transition metal, A is a group A element, and X is either C or N [6]. To produce MXene, the MAX phase is chemically etched, resulting in the selective etching of the A layers and their replacement with surface termination. Accordingly, their proper designation is Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} where T\textsubscript{x} consist of surface termination groups that include O, OH and F [7]. The resulting multilayer particles are weakly bound together and can subsequently be separated resulting in 2D metallic-like M\textsubscript{n–1}X\textsubscript{n}T\textsubscript{x} sheets.

MXene’s 2D nature, their good electronic conductivity [5], hydrophilicity in combination with the possibility to terminate their surfaces with various functional groups [2, 3, 8–10] and the ability to intercalate the MXene sheets [11, 12], render them highly attractive for, e.g. energy storage application such as Li-ion batteries [8, 11, 13, 14], and electrochemical capacitors [11, 15, 16]. From the number of MXenes produced to date (>20) in combination with the range of possible coordinations by surface terminating groups, the tailoring potential in this family of materials is noteworthy.

The coordination of the surface terminating groups on the MXene surfaces is predicted to strongly influence the material properties, including energy storage capacity [8], magnetism, band gap energy [9] and surface plasmon resonance [17, 18]. Depending on the chemical etching process, the composition of T\textsubscript{x} may vary significantly. However, unambiguous results

© 2017 IOP Publishing Ltd
on the identification and coordination of these surface-terminating groups have yet not been presented. Therefore, studying the coordination of \( T_x \) is a research topic of particular interest and importance. Density functional theory (DFT) calculations predict that of two possible sites for the \( T_x \) the A-site is the more energetically favorable \([9]\). The A-site is defined to be on top of the central Ti atoms, as shown in the plan- and cross-sectional views of the Ti\(_3\)C\(_2\)Tx structure presented in figures 1(a) and (b), respectively; the A-site in figure 1 is denoted by a circle. Included in figure 1 is also the B-site, which is defined to be on top of the central C atoms denoted in figure 1 by a square.

The deposition was performed using elemental Ti, \( Al \) and C targets with diameters of 75, 50 and 75 mm, respectively. Prior to deposition the substrate was preheated inside the deposition chamber at 780°C for 1 h. The Ti and C targets were ignited at 780°C with powers of 92 and 142 W, respectively, for 30 s forming an incubation layer of TiC before the Al target is ignited at a power of 26 W. The duration of sputtering is 10 min, which produces a film about 30 nm thick. Immediately after the Ti\(_3\)AlC\(_2\) thin film was removed from the PVD system it was converted into Ti\(_3\)C\(_2\)Tx by etching commercial Ti\(_2\)AlC\(_2\) powder with a particle size \(<38 \mu m\). The obtained powders were immersed in 10% HF(aq) in a ratio of 1 mg of Ti\(_3\)AlC\(_2\) to 20 ml of solution at RT for 24 h. The resulting suspension was washed with deionized water and separated from the remaining HF(aq) by centrifuging until the pH of the liquid reached a pH between 5 to 6. The separated powders were then finally washed with ethanol and left to dry overnight in air. TEM samples were thereafter prepared by crushing the powder in a mortar with a pestle and dispersing a mixture of the powder and ethanol on a DENSsolutions holey Si\(_3\)N\(_4\) Wildfire heater chip and placed in a DENSsolutions double tilt heating holder. Possible particles of Al\(_2\)O\(_3\) or other impurities were screened out in the process.

**Methods**

Thin film Ti\(_3\)C\(_2\)Tx samples used for the XPS measurements were prepared by first depositing Ti\(_3\)AlC\(_2\) on c-axis-oriented sapphire, Al\(_2\)O\(_3\), \(10 \times 10 \text{cm}^2\) surface area substrate using DC magnetron sputtering in an ultrahigh vacuum system. The deposition was performed using elemental Ti, Al and C targets with diameters of 75, 50 and 75 mm, respectively. Prior to deposition the substrate was preheated inside the deposition chamber at 780°C for 1 h. The Ti and C targets were ignited at 780°C with powers of 92 and 142 W, respectively, for 30 s forming an incubation layer of TiC before the Al target is ignited at a power of 26 W. The duration of sputtering is 10 min, which produces a film about 30 nm thick. Immediately after the Ti\(_3\)AlC\(_2\) thin film was removed from the PVD system it was converted into Ti\(_3\)C\(_2\)Tx by etching in 10% concentrated HF(aq) (Sigma Aldrich, Stockholm, Sweden) for 1 h at RT. After etching, the sample was rinsed in deionized water and ethanol. The etching and washing procedure used here has been demonstrated to result in a small increase in the lattice parameter because of the incorporation of the surface groups. Furthermore, the thickness of the film stays approximately the same after etching and washing. More details on sample preparation can be found elsewhere \([17]\). For this study it was important that the exposure to the atmosphere was kept as short as possible. The Ti\(_3\)C\(_2\)Tx sample was therefore placed in the XPS instrument shortly after the etching process was performed. Impurities, such as TiO\(_2\) and Al\(_2\)O\(_3\), and contamination, such as hydrocarbon and alcohol compounds, could thereby be kept at an insignificant level.

The Ti\(_3\)C\(_2\)Tx multilayered powder samples used for the STEM experiments were prepared by etching Ti\(_3\)AlC\(_2\) powders. The latter were synthesized by mixing commercial Ti\(_2\)AlC\(_2\) powders (Kanthal, Sweden, \(-325 \text{mesh}\)) with TiC (Alfa Aesar, Ward Hill, USA, 99.5 wt.% purity, \(-325 \text{mesh}\)) in a 1:1 molar ratio (after adjusting for the \(-12 \text{wt.}\%\) Ti\(_3\)AlC\(_2\) already present in the commercial Ti\(_2\)AlC powder) followed by ball milling for 18 h to ensure proper mixing. The powders were subsequently heated in a tube furnace to 1350°C with a rate of \(10^\circ\text{C min}^{-1}\) for 2 h under flowing Ar. The resulting material, in the form of a lightly sintered brick, was ground milled using a TiN-coated milling bit and sieved through a 400 mesh sieve, producing Ti\(_3\)AlC\(_2\) powder with a particle size \(<38 \mu m\). The TP-XPS was performed with the AXIS Ultra DLD system from Kratos Analytical Ltd using monochromatic Al K\(_\alpha\) radiation. The XPS was performed in an analyzer chamber while the temperature-controlled sample heating was performed in an adjoining

---

**Figure 1.** Schematics of the Ti\(_3\)C\(_2\) structure shown in (a) plan view and (b) cross-section. The suggested sites for the surface groups, \( T_x \) \([9]\), are indicated with a circle and a box.
I Persson et al. preparation chamber; both chambers had a base pressure better than $1 \times 10^{-9}$ mBar. The sample was heated to a given temperature for 0.5 h. It was then cooled and transferred from the preparation chamber into an adjoining analyzer chamber. After analysis the sample was transferred back to the preparation chamber and the process was repeated with steps of increasing temperatures until the maximum temperature of 750 °C was obtained. Since the sample was supported on an insulating sapphire substrate sample charging was a concern. To avoid inconvenient binding energy shifts caused by sample charging during spectra acquisition, potential depletion of electrons in the sample was compensated by a continuous flow of low energy electrons. The binding energy scale was calibrated against the Fermi-edge ($E_F$), which was set to a binding energy of 0 eV, and the overall energy resolution was better than 0.5 eV. Normalization of all spectra was performed at the background on the low binding energy side of the main peak/peaks. The TP-XPS was performed in the range of RT up to 750 °C.

The in situ heating experiments were performed inside the (S)TEM at temperatures ranging from RT to 750 °C using the same time steps as in the TP-XPS experiment. Characterization was performed using the Linköping double corrected FEI Titan3 60-300, equipped with a high-brightness gun (XFEG), monochromator, and Quantum ERS-GIF. High-resolution TEM images during in situ annealing were acquired at 60 kV. Thickness determination of the MXene sheets was performed through intensity variations in the STEM HAADF images. The high-resolution STEM images were acquired at 300 kV and <10 pA beam current. STEM image simulations (see supplementary information for details) were performed using the Dr Probe software [19]. STEM image analysis was carried out using built-in routines for the commercially available Digital Micrograph and Matlab (see supplementary information for details).

### Results and discussion

The aim of the present study is to provide experimental evidence on the identification and coordination regarding the termination groups on 2D sheets. It is therefore essential that the studied sample is kept as clean as possible, e.g. by reducing the exposure to the atmosphere to minimum duration. Owing to the extra precaution, contamination was found to be at an insignificant level. For example, figure S1 shows that the amounts of hydrocarbons and alcohol compounds are quite small and are estimated to be less than 3%. In addition, the TiO$_2$ contribution is also too low to be estimated. Comparison with previously presented XPS spectra of Ti$_3$C$_2$Tx [7] shows that the thin film Ti$_3$C$_2$Tx sample in the present work has significantly less impurities and contamination. Further discussion regarding sample impurities and contamination can be found in the supplementary information.

Figures 2(a)–(c) present, respectively, the F 1s, O 1s, and Ti 2p TP-XPS spectra of a Ti$_3$C$_2$Tx thin film on sapphire ranging from room temperature (RT) to 750 °C. As the temperature increases, the F 1s, O 1s, and Ti 2p spectra transform in response to changes in the quantities and coordinations of T$_x$. Most apparent is the loss in F 1s intensity (figure 2(a)) while the integrated intensity of the O 1s and Ti 2p spectra remain more or less constant throughout the TP-XPS study (see supplementary information figure S2).
The temperature-dependent intensity redistribution of the O 1s and Ti 2p provide valuable information about coordination sites for Ti on the Ti₃C₂ surfaces. The C 1s spectrum (shown in supplementary, figure S1) maintains a stable signal throughout the experiment, indicating that no loss of C occurs. More importantly, the stable C 1s signal at 282.0 eV indicates that the MXene does not undergo any reactions or phase transformations upon heating up to 750 °C.

The F 1s XPS spectrum at RT contains a single sharp peak at 685.3 eV, which indicates the existence of one F containing species that coordinates to a single site. The corresponding O 1s XPS spectrum contains two peaks centered at 529.9 and 531.9 eV, respectively suggesting two distinctly different surface O containing species or one species occupying two different sites. The Ti 2p XPS spectrum at RT shows the two spin–orbit split features 2p₃/2 and 2p₁/2 around 455.9 and 462.0 eV, respectively. A closer inspection suggests that the 2p₃/2 consists of two peaks separated by only about 1 eV indicating at least two different Ti coordinations, which the higher broadening of the 2p₁/2 cannot distinguish. The origin of the two Ti 2p₃/2 peaks, located around 455.1 and 455.9 eV, suggests that the Ti atoms are coordinated with two different termination groups.

Up to 500 °C the Ti₃C₂Tx sample is stable and the only change observed in the F 1s, O 1s, and Ti 2p TP-XPS spectra is the gradual intensity redistribution of the O 1s from 531.9 to 529.9 eV, i.e. from higher to lower binding energy peaks. In the 550–750 °C temperature interval, on the other hand, the F 1s peak intensity reduces to a fraction of its original intensity. Hence, F-species desorb from the Ti₃C₂ surfaces at elevated temperatures. More dramatic changes are also observed in the O 1s spectra where the peak at 529.9 eV is significantly reduced while a third peak grows at 531.3 eV; the latter dominates the O 1s spectrum after the 750 °C heat treatment. A parallel behavior is observed for the Ti 2p peak where the intensity redistribution benefits the growth of the Ti 2p₃/2 peak at 455.1 eV and Ti 2p₁/2 peak at 461.2 eV.

The Ti 2p spectra in figure 2 shows that the F desorption process is not complete even after the 750 °C heat treatment and the O 1s and Ti 2p spectra therefore still show the 529.9 and 455.9 eV features as shoulders on the main peaks. Nevertheless, the sharp O 1s and Ti 2p₃/2 main peaks at 531.3 and 455.1 eV, respectively, implies that there is only one surface group that prevails after a thorough high-temperature heat treatment in vacuum. In addition, the fact that the reduction in the F 1s intensity coincides with the decrease in the Ti 2p₃/2 intensity around 455.9 eV suggests that the high binding energy Ti 2p₃/2 feature originates from Ti with adsorbed F, which implies that the Ti 2p₃/2 peak at 455.1 eV originates from Ti with adsorbed O species, as is expected from the HF(aq) etching [2, 3], and possibly uncoordinated Ti. However, the sharp Ti 2p₃/2 and O 1s peaks at 455.1 and 531.3 eV, respectively, indicate that after the heat treatment at 750 °C, i.e. after most of the F has desorbed, the O containing species can only be either O or OH. That means that if both O and OH are present as surface terminating groups in the etching process, then one of them must desorb or transform into the other during the heat treatment. It is feasible that the broad Ti 2p₃/2 peak at RT could consist of three features, although any proposed third peak must: (i) be stable up to but, (ii) start to reduce in intensity at the same temperature as the F starts to desorb. More information can, on the other hand, be gained from the O 1s spectrum. The integrated intensity for the O 1s spectra does not change significantly during the study, from which one can infer that no O-containing species has desorbed from the Ti₃C₂ surface. (The integrated intensity for F 1s, O 1s, Ti 2p, and C 1s spectra of Ti₃C₂Tx ranging from RT to 750 °C is shown in supplementary information figure S2.)

Moreover, the absence of an integrated intensity reduction of the O 1s TP-XPS spectra implies that an OH dissociation has not occurred, because were that the case the dissociation product H would react with neighboring OH and form H₂O that would desorb immediately at temperatures above 500 °C and decrease the integrated intensity of the O 1s spectra accordingly. Hence, a significant transformation from OH into O can be excluded. In addition, a transformation from O into OH can also be removed from consideration because that would require a substantial amount of hydrogen supplied to the Ti₃C₂ surface. Consequently, there can only be one O containing species introduced at the etching process and that species stays intact throughout the heat treatment up to 750 °C. The instability of OH on Ti surfaces at higher temperatures [20] (O 1s integrated intensity is expected to diminish), the fact that surface OH is prone to react and form water that would later desorb (reducing the O 1s signal), and that OH is in general not very mobile (O 1s signal should exhibit no peak shifts in the TP-XPS) are three contradictions to what we observe in our XPS data. This leads us to conclude that little or no OH is present on the Ti₃C₂Tx surface. Altogether, the information gained from the TP-XPS study indicates that the single O containing species is atomic oxygen that is mobile on the Ti₃C₂ surface, can occupy two adsorption sites on the Ti₃C₂ surface, and is stable at temperatures up to 750 °C.

The peak positions and intensity redistribution observed in the TP-XPS study implies that the F is adsorbed on one specific and well-defined site on the Ti₃C₂ surface and that O is adsorbed on two different sites where one is the same preferred adsorption site as for the adsorbed F. It is proposed that during the HF(aq) etching of Ti₃AlC₂, the F and O atoms compete over the same preferred site on the Ti₃C₂ surface. While F occupies only one adsorption site, O resides on two alternative sites. The O 1s intensity redistribution in the temperature interval of 300–500 °C suggests that O on the preferred absorption site moves to the alternative site because of influences from F, i.e. charge
transfer from Ti to the adsorbed F makes the preferred site less attractive for the adsorbed O. Said otherwise, Ti$_3$C$_2$ surface favors adsorbed F on this specific site and the less favored O is relegated to the alternative site. However, when F desorbs, at temperatures above 550 °C, the preferred site becomes available and a complete redistribution follows when O rearranges from the alternative site to the preferred.

The intensity redistribution of the Ti 2p peaks reveals a charge transfer from the adsorbed F back to Ti$_3$C$_2$ prior to F desorption (the shoulder at 455.9 eV diminishes while the intensity at 455.1 eV increases after F desorption). With the highest electronegativity of all elements, F attracts significantly more electrons from the Ti$_3$C$_2$ as compared to O. The consequence is an uneven charge distribution with reduced electron density on the Ti atoms coordinated to F compared with Ti atoms that are not. The local electron density valleys, which are positive with respect to the surroundings, will attract delocalized electrons in order to screen it, which causes a strengthening of the covalent Ti–C bonds in Ti$_3$C$_2$ \[21, 22\]. This charge transfer from the Ti atoms to the adsorbed F, and consequently the distribution of the delocalized electrons, presumably causes a relatively reduced charge transfer to the O adsorbed on the preferred site when O is co-adsorbed with F compared to the charge transfer to the adsorbed O from the Ti$_3$C$_2$ surface after the F has been desorbed. This is proposed here as the reason why the high binding energy peak in the O 1s spectra shifts −0.4 eV when the situation for O on the Ti$_3$C$_2$ surface changes from being co-adsorbed with F to being the sole terminating group.

The TP-XPS shows that there is a preferred absorption site for the F and O atoms and that O also (while F is in the preferred site) occupies an alternative site. The observations that (i) the Ti 2p peaks go through a significant intensity redistribution upon desorption of F, (ii) the C 1s peak do not show any significant binding energy shifts (figure S1), and (iii) the origin of the high binding energy peak in the O 1s spectrum is the preferred site, and that the two O 1s peaks are separated by ~1.5 eV, suggests that the preferred absorption site for both F and O might be, e.g. a hollow site and the alternative O site, e.g. a bridge site \[23\]. To confirm this, a corresponding high-temperature investigation was performed inside the (S)TEM.

Figure 3 shows sequential TEM images from a corner of a MXene multilayer particle as a function of increasing temperatures (see Methods for details on synthesis). At ambient temperature, disorder is strongly visible in addition to the ordered structure of the MXene sheets, see figure 3(a). The disordered material is interpreted as a mixture of C-based molecules that originate from the TEM sample preparation procedure and adsorbed functional groups originating from the HF(aq) etching process. The majority of the C-based molecules are removed at temperatures slightly above 100 °C. Hence, the 300 °C image in figure 3(b) appears slightly cleaner, although disorder is still present. The images at 400 and 500 °C in figures 3(c), (d) show a similar appearance, marginally improving with temperature. However, at 600 °C and in particular at 700 °C, the image indicates that the particle appearance is significantly affected by the applied heating. Most notable is the improvement in the thinnest regions and at the edges (interfacing vacuum), that assume a distinctly faceted outline. Additionally, the image now visibly demonstrates Fresnel
contrast based dark lines that outline the surface steps, between the various MXene layers, which run alongside the outline of the particle. Most importantly, the structure has assumed a significantly crisper appearance and the initial disorder is lost.

Fast Fourier transformations (not shown) of the images indicate that the MXene structure itself has not undergone any phase changes, which can also be understood from the preservation of the microstructural features. It is recalled that TP-XPS showed no loss of Ti, C or O although a significant reduction of F from the Ti$_3$C$_2$ surface was observed. Consequently, the observed changes through the image series are attributed to the reduction of F and the reorganization of O atoms.

To investigate the organization further, and to identify the atomic structure of the heat-treated MXene, high-resolution STEM imaging was performed on a single sheet at elevated temperatures. The plan-view image that is shown in figure 4 was acquired at 500 $^\circ$C, after pre-heating up to 700 $^\circ$C for 30 min (instabilities at temperatures $>500$ $^\circ$C caused difficulties in acquiring high-resolution images). The image reveals patches of different intensities and symmetries. A closer inspection of these areas further identifies different surface patterns as exemplified in figures 5(a)–(d). Intensity normalization was performed on the tails extending into vacuum; more details are given in the supplementary material. The least intense areas shown in figure 5(a), exhibit a weakly increased intensity at every third projected atom column and forms a more sparsely occupied close packed structure compared to the MXene as exemplified in figure 5(c) (peak intensity positions exhibit a red color, while background peak positions are blue–green). In figure 5(b) the pattern is similar, although the average intensity is higher with peak intensity columns in the red–yellow range. The pattern in figure 5(c), with a slightly increased background intensity compared to that in figure 5(a), exhibits high intensity atomic columns organized in a honeycomb-like pattern. These columns additionally surround a slightly less intense column. Through close inspection it is revealed that every second atomic position of the honeycomb hexagon exhibits a faintly elevated intensity over the neighboring high intensity positions. The background intensity additionally varies in the image, e.g. the honeycomb structure centered in the image exhibits a higher intensity compared to the adjacent honeycomb at the bottom right. Finally, the image in figure 5(d) exhibits brighter features that also form a honeycomb-like structure, similar to figure 5(c), on an additionally increased intensity background.

In order to interpret these different patterns, we simulated various STEM images as a function of surface termination and their distributions and the results are shown as insets in figure 5 (additional simulations are shown in the supplementary material). The structures considered for the simulated insets are shown in figure 6. This includes; (a) a single bare (T$_x$-free) Ti$_3$C$_2$ MXene sheet, (b) O coverage on the bottom of a Ti$_3$C$_2$ sheet (i.e. on the exit wave surface), (c) O on top (i.e. facing the electron beam) and, (d) O coverage on both surfaces. The proposed O site (A-site, see figure 1) stems from previous work where x-ray and neutron scattering atomic pair distribution func-
tion experiments were used to determining the bond lengths of Ti–C/O/F in Ti$_3$C$_2$Tx MXenes [24, 25]. Other possible sites for O were additionally considered but were ruled out after comparison to the experimental images and for symmetry reasons (O should choose equivalent positions on both surfaces). The surface models were matched quantitatively by comparing atomic column intensity levels and additionally by intensity pattern distributions of neighboring columns. For a more detailed discussion see supplementary material (figures S11 and S12). Notably, the atomic column intensity does not reflect the commonly generalized Z$^2$ scattered intensity for atomically resolved STEM images [26]. This is particularly visible for the bare MXene. By comparing to the structure model applied in this simulation (inset in figure 5(a)), the projected column that includes Ti1 and C1 atoms (column $\alpha$ in figure 6(a)) returns the highest intensity and forms a sparse close packed appearance. In contrast, the projected column containing C2 and Ti3 atoms (column $\gamma$ in figure 6(a)) returns the lowest intensity. The Ti2 layer (projected column $\beta$ in figure 6(a)) returns an intermediate intensity. The mechanism behind the different contrast is further discussed in the supplementary material. Astonishingly, the simulated images indicate that it is possible to identify the top and bottom surfaces of the sheet, simply through intensity variations. Comparing the simulated bare MXene in figure 5(a) with the low intensity regions represented in the experimental image the structure matches qualitatively, which, indicates that these low intensity regions constitute bare Ti$_3$C$_2$ areas. In air and at ambient conditions, this state would be remarkable; it is less so in the ultrahigh vacuum environment of the TEM after heating to 750 °C.

The simulated image in figure 5(b) comprise a single sheet MXene covered with O adatoms on the A-sites (figure 6(b)) on the bottom surface. In analogy with the intensity of the exit surface Ti3 atoms, the lower mass of bottom surface O adatoms add little contrast to the simulated image individually. However, the background intensity of the simulated image has increased, raising the intensity of all atomic columns. Again, the most intense columns correspond to those that include the Ti1 atoms, and the results compare well with the observed background intensity increase observed in figure 5(b).

Figure 5(d) shows the results from a simulation exhibiting O adatoms on A positions on both surfaces. The honeycomb pattern is preserved, however the background intensity is further elevated and the highest intensity columns here correspond to columns containing the O adatom on the top surface. The simulation results as shown in the insets in figures 5(c) and (d), indicate that the varying intensity of the honeycomb pattern observed in figure 5(c) is the result of partial O coverage on both surfaces. The honeycomb patterns observed across figure 4, hence serve as distinct fingerprints of the preferred O position after high-temperature heating. Simulations for other configurations were performed but failed to return the honeycomb pattern (figures S7(d) and (e)). Consequently, this indisputably verifies the A-site as the preferred position for the O adatom in total accord with the XPS results.

Locally, figure 4 additionally displays even brighter atomic positions. These positions are after simulation (supplementary information figure S6) interpreted as Ti adatoms. The darkest intensities in the sheet are interpreted as Ti vacancies. Statistical analysis further supports this interpretation by the observed approximately 1:1 ratio of darkest lattice positions and brightest lattice positions (Ti vacancies and Ti adatoms).

The identification and favored position of the surface groups $T_x$ is essential information for a comprehensive understanding and control of MXene properties, such as charge capacity and ion mobility.
O surface adatoms are highly mobile on Ti₃C₂ surfaces. In this work we reveal, for the first time, the preferred positions of the O and F surface adatoms by employing a combined temperature-programmed XPS and direct observation high-resolution (S)TEM imaging of TiₓCᵧTₓ. It is found that the F terminations only occupy A-sites and that the O atom preferably occupies the same site as F takes precedence over O. Thus, while the F atoms occupy the preferred site, the O also resides on an alternative site, which presumably causes the apparent disorder observed prior to heating (figure 3(a)). This alternative site remains unidentified though it is proposed to be a bridge site. It has been observed that O surface adatoms are highly mobile on TiₓCᵧ surfaces even at ambient temperatures [29]. This may indicate that the alternative site exhibits a low binding energy, as discussed in the results, contributing to the observed disorder. In contrast, the surface configuration after heating to 750 °C is highly stable, even at the 500 °C elevated temperature used during image acquisition, shown in figure 4.

In a previous XPS work [7], peaks between 531.2 eV and 532.0 eV were assigned to C–Ti–O, C–Ti–OHₓ, bridging OH groups on TiO₂, and/or organic compounds. Based on the present work all these peaks can be assigned to atomic O sitting on the thermodynamically preferred A-site with small variations in the local bond configuration. Furthermore, based on the results shown herein and in total agreement with the finding that at the highest temperatures the O occupies the A-sites, we can more confidently propose the peak at 529.9 eV to atomic O bridging two Ti sites on the MXene surface and not a TiO₂ surface. This finding contradicts the majority of reports in the field, which consider OH termination to be the more likely functional group. However, in agreement with the present work, a recent NMR investigation identifies O to be the dominant functionalizing element on TiₓCᵧ surfaces [30].

With the HAADF-STEM identification of preferred terminations in mind, it is motivated to perform curve fitting of the XPS spectra, as shown in figure S1(b). The curve fitting of the F 1s spectra requires two curves at 684.5 and 685.3 eV to fit the slight asymmetry of the spectrum profile. The former is suggested to represent F occupying the A-site without influences from other adsorbates while the latter, the main component of F 1s, represent influences from co-adsorbed O. The O 1s spectra are curved fitted with two or three curves. The curves at 529.9 and 531.9 eV originate from adsorbed O at the alternative site and at the preferred A-site, respectively. The high binding energy curve is relatively broad, which indicates different local environment of the probed O atoms on the A-site. This is a consequence of the highly mobile O on the TiₓCᵧ surface [29] and that O is co-adsorbed with F in different local bond configurations. However, at temperatures above 600 °C a third curve at 531.3 eV is required. This curve represents O on A-sites that are not influenced by co-adsorbed F. The Ti 2p spectra are curved fitted with three pairs of curves. The three curves that represent the Ti 2p₁/₂ are at 455.1, 455.9, and 456.9 eV and the corresponding curves for the Ti 2p₃/₂ are at 461.2, 462.0, and 463.0 eV. The pair of curves at 455.1 and 461.2 eV originates from Ti with a local adsorption of only O, while the pair of curves at 456.9 and 463.0 eV originates from Ti with a local adsorption of only F. The pair of curves at 455.9 and 462.0 eV originate from Ti with a local environment that is influenced from both F and O.

The curve fitting of the Ti 2p XPS spectra can be illustrated as shown in figures 6(e)–(h). These figures identify O or F adatoms on A-sites surrounding a TiI atom (in this top-view projection). Each surface TiI is surrounded by a combination of three F and O atoms: O–O–O (denoted TiₓCᵧTₒ), O–F–O and F–O–F (denoted TiₓCᵧTₒF), and F–F–F (denoted TiₓCᵧT₃). Hence, Ti atoms can be affected by only O, only F, or both F and O. The asym-GL curve that fits the Ti 2p₁/₂ peak at 455.1 eV originates from TiₓCᵧTₒ. The other curves are related to Ti atoms that are affected by the adsorbed F occupying the A-site as in figures 6(f)–(h). When Ti atoms are affected by both F and O, the Ti 2p₁/₂ is shifted by 0.8 eV and when Ti atoms are affected by only F (figure 6(h)) the Ti 2p₁/₂ is shifted further to 456.9 eV. These chemical shifts can be explained by the higher electronegativity of F compared to O which attracts significantly more electrons from the TiₓCᵧ sheet. Potentially, small chemical shifts also exist between Ti atoms with F–O–F and O–F–O configurations that would require additional curves for a more accurate curve fitting of the Ti 2p₁/₂. Even further combinations are possible if the influences from the O atoms on the alternative site are included or if there are vacancies in the F and O adsorbate structures. Nevertheless, details of the F and O combinations on the A-sites and the influences from the O adsorbed on the alternative site are not obtained in this work, although the two curves representing TiₓCᵧTₒO and TiₓCᵧTₒF have relatively larger FWHM, compared to the curve representing TiₓCᵧTₒ suggesting that the F related Ti 2p₁/₂ feature around 455.9 eV could very well consist of more than two components, separated by only a few tenth of an eV.

The obtained parameters from the curve fitting of the F 1s, O 1s, and Ti 2p XPS spectra are summarized in table 1. Included are also the obtained parameters from the curve fitting of the C 1s XPS spectra (see figure S1(a)). This investigation also reveals that a high-temperature heating process can be utilized to rid the MXene surfaces from F, and to organize available O onto the A-sites. These results suggest that a chemical etching process that functionalizes the MXene surfaces by a high amount of F adatoms can be used together with a subsequent high-temperature heating to produce
Conclusions

In conclusion, the organization of surface groups on Ti3C2Tx MXene was investigated as a function of temperature. Through temperature-programmed XPS it was shown that the functional groups consist of F and O occupying well-defined sites on the Ti3C2 surfaces. While the functional F coordinates to a single site, the functional O coordinates to two sites. As the temperature exceeds 550 °C, the functional F gradually desorbs and is essentially removed at 750 °C. Upon F desorption the O surface atoms that coordinates to the alternative site, which most likely is a bridge position, migrate to the preferred coordination vacated by the desorbed F.

In situ heating of a few layers of Ti3C2Tx sheets in the TEM shows that the initial surface disorder transforms into highly ordered structures at temperatures corresponding to the reconfiguration temperatures observed by the TP-XPS. In addition, through high-resolution STEM imaging and corroborating STEM image simulations the functional O atoms were found to thermodynamically favor the A-sites, i.e. on top of the Ti atoms of the middle layer. Hence, the MXene heating process is suggested to be vital for further research efforts as it enables surfaces with well defined coordinations. It also leaves part of the MXene surface bare and unfunctionalized, such that further functionalization can be introduced. The heating process may thus serve as a route towards manipulating the functionalization of MXene surfaces. Together, these findings would prove valuable towards improved performance for MXene materials in, e.g. supercapacitor and battery applications.

Acknowledgments

The authors acknowledge the Swedish Research Council for funding under grants no. 621-2012-4359, 622-2008-405, 2013-5580, 2016-04412, 642-2013-8020, and the Knut and Alice Wallenberg’s Foundation for support of the electron microscopy laboratory in Linköping, for project funding (KAW 2015.0043), and a Fellowship program. The authors also acknowledge Swedish Foundation for Strategic Research (SSF) through the Synergy Grant FUNCASE, Future Research Leader program and the Research Infrastructure Fellow program (RIF14-0074). The authors additionally acknowledge support from the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No 2009 00971).

Supporting information

Detailed experimental procedures, XPS data and curve fitting, TEM images, and interpretation are presented.

Author contributions

J H carried out the growth. I-Å N performed the XPS experiments and analysis. I P, J P, P O Å P performed the TEM/STEM experiments. I P conducted the STEM simulations. I P, J P, P O Å P performed the TEM/STEM analysis. I P, I-Å N, P O Å P prepared the manuscript. All authors assisted in finalizing the manuscript. M W, B, V D, J R, J P, P O Å P supervised the work.

Notes

The authors declare no competing financial interest.

ORCID iDs

Per O Å Persson  https://orcid.org/0000-0001-9140-6724


References

[19] Barthe I 2016 Dr. Probe-STEM simulation software (www.er-c.org/barthel/drprobe/)