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# Atomic-scale investigations of $Ti_3C_2T_x$ MXene surfaces

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## SUMMARY

The family of two-dimensional (2D) carbides and/or nitrides, also known as MXenes, have generated great excitement within the scientific community and have been proposed for a wide variety of applications since their discovery. Despite this attention, there have been only limited studies of the atomically resolved local electronic and physical structure of MXene surfaces strongly affecting the physicochemical properties of these materials. Here, we report local structural, spectroscopic, and chemical investigations of the surfaces of  $\text{Ti}_3\text{C}_2\text{T}_x$  flakes using scanning tunneling microscopy and spectroscopy, closely coupled to theoretical studies. Terminal groups are visualized and characterized, along with surface  $\text{TiO}_2$  clusters formed upon exposure to air. Fundamental insight into

the local electronic and chemical properties associated with different terminal groups on MXenes and their oxidation products is presented.

## INTRODUCTION

Since their discovery in 2011,<sup>1</sup> transition metal carbides and/or nitrides, also known as MXenes, have attracted great attention, because of their versatile physicochemical properties, which pave the way for their use in a broad range of applications, spanning from biomedicine and energy storage to electronics, catalysis, and sensing.<sup>2</sup> MXenes have a general formula  $M_{n+1}X_nT_x$ , with  $n$  being an integer from 1 to 4,  $M$  denotes an early transition metal and  $X$  is carbon and/or nitrogen (can be substituted for oxygen).  $T_x$  describes the surface terminations, where  $x$  is a variable representing the possible terminations. In the case of the wet chemical synthesis used in this study, the terminal groups are a mixture of =O, -OH, and -F, as shown in **Figure 1**). The relative ratio of terminations varies as a function of the synthesis process and post-treatment (washing, drying, and aging in air), which we use to our advantage. Here, we took the nominal MXene composition  $Ti_3C_2O_{0.48}OH_{1.04}F_{0.48}$ .<sup>3</sup> Systematically varying this ratio by using different processing conditions enables us to identify functional groups in spectroscopic imaging and local spectroscopies, in combination with calculated spectra (*vide infra*).

The unique and highly tunable properties of MXenes make them prime candidates for boosting current technologies as well as enabling breakthroughs in many research fields.<sup>4</sup> Much of MXenes' potential results from their rich surface chemistry. The charge carriers responsible for MXene's optical properties and electronic transport are close to its external interfaces. Depending on the MXene composition, the carrier plasma may be either sensitive to or uncommonly robust against the resulting changes in the band structure and state-filling. Atomic-scale control of surface chemistry ( $T_x$ ) enables fine-tuning of their optical and electronic properties, influencing material interactions with electromagnetic waves and affecting the ultimate material and device performance.<sup>5-8</sup> In this regard, exploring and controlling the MXene surface chemistry at the atomic scale is crucial and many efforts have targeted this goal.<sup>9,10</sup> In those studies, analyses of MXene surfaces used transmission electron microscopy (TEM) and electron energy loss spectroscopy,<sup>7</sup> atomic-layer-by-atomic-layer secondary ions mass spectrometry (SIMS),<sup>11</sup> and tip-enhanced Raman spectroscopy (TERS).<sup>12</sup> The SIMS and TERS techniques do not offer atomic resolution, and TEM analysis is inefficient for resolving the local surface structure of 2D flakes with several atomic layers, even though defects and adatoms can be observed using TEM.<sup>13</sup> Scanning probe microscopy techniques providing atomic-scale resolution have been developed and used to unveil surface features of many 2D

materials, including graphene.<sup>14–18</sup> In particular, scanning tunneling microscopy (STM) and spectroscopy techniques were instrumental in studying the surfaces of conducting, semiconducting, and semi-metal 2D materials, such as graphite, graphene, MoS<sub>2</sub>, etc.<sup>19,20</sup> While most MXenes have metallic conductivity and could potentially be studied by STM, to date, there are few literature reports of STM images of MXenes.<sup>21</sup> The combination of STM and scanning tunneling spectroscopy (STS) analyses can elucidate electronic properties and states with high spatial resolution in real space, as well as detailed information about the nature and distribution of surface functional groups. Here, for the first time, we report a thorough STM/STS analysis of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene, performing local structural, spectroscopic, and chemical investigations of its surface with sub-nanometer resolution. Our findings pave the way for unveiling, at the atomic level, the surface chemistry of MXenes and its influence on the local density of states, thereby leading to understanding of key function through structure-property relationships.

## RESULTS

Scanning tunneling spectroscopy data were collected using a method described previously in the literature.<sup>22</sup> More detailed descriptions of data treatment and the associated raw data are given in the Supplemental Information (**Figures S3-S24**). Both

ambient and low-temperature (LT) ultrahigh vacuum (UHV) STM images were recorded for  $\text{Ti}_3\text{C}_2\text{T}_x$  flakes on Au{111} (**Figure 1b**). Ambient imaging revealed protrusions on the surface but lacked sufficient resolution for detailed studies. The LT UHV STM imaging revealed small clusters, on the order of 10 nm across, on the surface (likely titanium oxide), as shown in **Figure 2b**, and protrusions on the order of 0.5 nm that we assign to be terminal groups functionalizing the surface (*vide infra*), as shown in **Figure 2c**. The functional groups display distorted hexagonal symmetry, consistent with the loss of symmetry on the surface due to nonuniformly distributed surface terminations (O, OH, and F). Our simulated STM images (**Figure S2a**) also featured similar distorted hexagonal symmetry. From the surface terminations (O, OH, and F) distribution (**Figure S2b**), these protrusions are likely due to hydroxyl (-OH) groups, with nearest neighbor distances of ~1.2 nm, consistent with the observations in **Figure 2c**. Similar distortion was seen in TEM studies upon oxidation and annealing of MXenes.<sup>23</sup> For UHV STM studies, one often needs to anneal samples at elevated temperatures to remove physisorbed water and contaminants. Annealing beyond 320 °C leads to a release of entrapped water, and terminal group dissociation starts around 530 °C.<sup>24</sup> We partially attribute the disorder on the surface to this treatment, as the samples were annealed to ~490 °C in UHV, but terminal group composition should not have changed. Based on theory and prior literature, we tentatively assign this terminal functionality as hydroxyl groups.<sup>23,25</sup>

Scanning tunneling spectroscopy data were collected at the points indicated in **Figure 2d** and are shown in **Figure 2e, f**. Both the  $I$ - $V$  and  $dI/dV$  spectra indicate that the surface is metallic, consistent with previous literature,<sup>26,27</sup> and the calculations performed in this study. These spectra are easily differentiable from the spectra for the bare Au{111}, where surface states are observed (see Supplemental Information **Figure S26**).

We have performed density functional theory (DFT) modeling of various surface termination configurations adopted from ref <sup>3,28</sup> on Au substrate, to couple with the experimental observations. The  $I$ - $V$  characteristics of the  $\text{Ti}_3\text{C}_2\text{T}_x/\text{Au}$  are calculated using the Tersoff and Hamann formalism<sup>29</sup> by taking the thermally excited electrons into account, as proposed by He et al.<sup>30</sup> We find that by varying the ratio of the surface termination groups,<sup>3</sup> one can tune the electronic conductivity of the system. As shown in **Figure 3a**, the calculated electron density of states (eDOS) at the Fermi level,  $E_F$  varies with respect to the O/OH/F composition ratio of  $\text{Ti}_3\text{C}_2\text{T}_x$ . For both the mixed terminated and uniformly O-/OH-/F-terminated surface (see Figure S25), an OH-rich surface would result in a higher eDOS at  $E_F$ , whereas an O-rich surface exhibits a lower eDOS at  $E_F$ . This trend is consistent with the simulated STS shown in **Figure 3b,c**. Higher current ( $I$ - $V$ ) and differential conductance ( $dI/dV$ ) have been observed for an OH-rich surface. Besides eDOS at  $E_F$ , the variation of work function as a function of terminating group ratio on



$\text{Ti}_3\text{C}_2\text{T}_x$  observed from a recent study<sup>3</sup> can also explain the trends observed in **Figure 3b,c**. The calculated work function varied from the lowest to the highest when the surface transitioned from an OH-rich to an O-rich surface, which would substantially influence the magnitude of the tunneling current, as indicated in the tunneling current based on Tersoff and Hamann formalism (see the equation in the Computational methods and details in SI). Thus, in general, a mixed terminated OH-rich  $\text{Ti}_3\text{C}_2\text{T}_x$  surface, with a lower work function, would facilitate tunneling from the surface when bias is applied, leading to higher current and conductance.

From our previous theoretical studies of the effects of the surface distributions of terminal groups (O, OH, F) on the structural and electronic properties of  $\text{Ti}_3\text{C}_2\text{T}_x$ ,<sup>28</sup> we found that the distribution of surface terminal groups has minimal effect on the thermodynamic stability of  $\text{Ti}_3\text{C}_2\text{T}_x$  for a given stoichiometry, in which distinct distributions of terminal groups (e.g., ordered distributions, where terminal groups form local clusters, in comparison with random distributions, where terminal groups are distributed randomly on the surface) are thermodynamically degenerate. In addition, distinct terminal group distributions yield similar electronic properties, particularly the electronic DOS and work function.<sup>28</sup> As the work function and electronic DOS are a function of  $T_x$  stoichiometry instead of the terminal group distribution, we expect the STS results to be comparable and similar if considering different distributions for a given stoichiometry.

High-resolution STS spectra were recorded at two points marked in **Figure 4a** with the  $I$ - $V$  and  $dI/dV$  shown in **Figure 4b, c**. The black spectra recorded in between protrusions show metallic character consistent with measurements on bare  $\text{Ti}_3\text{C}_2\text{T}_x$  surfaces. The red spectra, recorded at an apparent protrusion with a lower apparent height that is most visible in **Figure 4d**, reveal two peaks in close proximity to the Fermi level at sample bias voltages of -10 and +10 mV. Differential conductivity maps were recorded in the area shown by the dashed white box in **Figure 4a** and are shown in **Figure 4d, e**. Here, higher intensity protrusions show an increased local DOS above and below the Fermi level, which is consistent with the acquired point STS. This increase in the local DOS can be explained by our simulations in **Figure 3**, where local variation in surface terminations yield a difference in the number of available electronic states. Local measurements help visualize a highly tunable MXene surface, where terminal groups drive changes in electronic conductivity.

Given that samples were allowed to oxidize in contact with the ambient atmosphere, we investigated the electronic effects of this oxidation on the  $\text{Ti}_3\text{C}_2\text{T}_x$  surface. Previous studies have found that nanoscale  $\text{TiO}_2$  clusters form on  $\text{Ti}_3\text{C}_2\text{T}_x$  with exposure to air.<sup>31-33</sup> They can serve as precursors to titania nanocrystals visible as protruding speckles

(displayed as white) in **Figure 1d**. An oxidized cluster was identified at the top of **Figure 5a** (highlighted by a green line) using STM and STS combined with the calculated spectra. Differential conductivity spectra were recorded along the green line to map the effect of oxidation on the electronic structure and are shown in **Figure 5b**. Metallic character is seen at either end of the line, but over the oxidized cluster, we find that a band gap has opened. These results are consistent with theoretical calculations of a similar but smaller cluster on  $\text{Ti}_3\text{C}_2\text{T}_x$  on Au, shown in **Figure 5c**. In the theoretical simulation, the calculation was performed with a  $\text{TiO}_2$  cluster ( $\sim 8$  Å in size) presented on the mixed terminated OH-rich  $\text{Ti}_3\text{C}_2\text{T}_x$  surface as demonstrated in the inset of **Figure 5c**. Our calculation shows that such a free  $\text{TiO}_2$  cluster (with a wide bandgap of  $\sim 2$  eV when not on a metallic surface, see **Figure S65**) could explain the significant suppression of the conductance when an oxidized cluster is present on the  $\text{Ti}_3\text{C}_2\text{T}_x$  surface, despite the overall system remaining metallic. Note that in our simulation model, the  $\text{TiO}_2$  cluster is nearly 10 times smaller than what was observed in **Figure 5a** (7.3 nm). Nevertheless, even with the presence of such a small semiconducting  $\text{TiO}_2$  cluster, the conductance is readily decreased (**Figure 5c**) compared to the non-oxidized  $\text{Ti}_3\text{C}_2\text{T}_x$ . Previous experimental studies have shown that the oxidation of  $\text{Ti}_3\text{C}_2\text{T}_x$  nanosheets would yield substantial degradation in the structural stability and conductivity<sup>31,34</sup> of the MXene sheets, suggesting that changes in the electrical properties would be expected upon the oxidation of the MXene.

## DISCUSSION

The band gap observed here is smaller than previous reports.<sup>33</sup> There are several possible explanations for this discrepancy, one of which is thermal broadening effects, which scale with  $\sim 3k_B T$ . Our measurements were recorded at 4 K, leading to a peak width of  $\sim 1$  meV compared to  $\sim 80$  meV at room temperature.<sup>35</sup> The size of the cluster, defect density, and effects of the MXene flake substrate also may affect the band gap and available electronic states, paving the way for future investigations.

Demonstration of successful use of the STM STS techniques to studying the most common MXene,  $Ti_3C_2T_x$ , with mixed surface terminations, opens the path to using the same approach to characterize termination-free, halogen-, and chalcogen-terminated MXenes.<sup>36,37</sup> Also, MXenes beyond  $Ti_3C_2T_x$  should be studied to understand their surface chemistry, defects, and local electronic properties.

## CONCLUSIONS AND PROSPECTS

While  $Ti_3C_2T_x$  is the most widely studied MXene, there have not been detailed local electronic and chemical structural investigations reported. The high-resolution investigations of terminal functional groups on  $Ti_3C_2T_x$  via STM, STS, and DFT reported in this study give new insight into the fundamental electronic properties and structure of

these important 2D materials. Theoretical calculation of the electronic structures and STS spectra in this work provides a baseline model to explain the difference in the  $I$ - $V$  and  $dI/dV$  characteristics of oxidized and non-oxidized surfaces on  $\text{Ti}_3\text{C}_2\text{T}_x$ . The work detailed here provides a starting point for further atomic-scale explorations of MXenes and their derivatives using STM and other surface probe microscopy and spectroscopy techniques. While sample preparation methods remain a challenge in the production of pristine  $\text{Ti}_3\text{C}_2\text{T}_x$  samples for their use in cryogenic experiments, in real-world applications, the functionalization and oxidation of MXenes, as studied here, are important factors to consider in their use.

## EXPERIMENTAL PROCEDURES

Resource Availability

Lead Contact

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Materials Availability

Samples of the MXenes used in this study are available upon request from the Gogotsi laboratory at Drexel University.

Data and Code Availability

Scanning tunneling microscopy and spectroscopy data are available from the Weiss laboratory at UCLA and are detailed in the supplementary information. The data and calculation details are available from the Lau laboratory at CSUN.

## Materials and Methods

### Synthesis of MXene

One gram of High-Al  $\text{Ti}_3\text{AlC}_2$  MAX powder (synthesized following our previously reported protocols<sup>S1</sup>) was slowly added to a 20 mL mixture of concentrated HF (49 wt %), concentrated HCl (36 wt %), and DI water, with a volumetric ratio of 1:6:3. The MAX phase was etched at 35 °C for 72 h. After the reaction was completed, the etching product was washed with DI water via multiple centrifugation steps (3500 rpm, 5 min) until neutral pH. In order to delaminate the MXene sheets, the  $\text{Ti}_3\text{C}_2\text{T}_x$  multilayer product was stirred at 300 rpm in a 50 ml aqueous solution containing 1 g of LiCl, at 35 °C for 18 h. Then, LiCl was removed from the solution by a single centrifugation step (3500 rpm, 5 min), discarding the clear supernatant. After that, the  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene was completely redispersed in water via shaking and centrifuged for 15 min at 3500 rpm (to precipitate the multilayer MXene and unreacted MAX particles). Finally, the dark supernatant — containing single-layer MXene sheets — was collected.

### Scanning tunneling microscopy sample preparation

Au{111}/mica substrates (Keysight Technologies, Santa Rosa, CA) were hydrogen-flame annealed with 10 passes at a rate of 0.4 Hz and exposed to oxygen plasma for 5 min prior to use. Samples were prepared according to literature precedent using freshly prepared  $\text{Ti}_3\text{C}_2\text{T}_x$  solution in water.<sup>S2</sup> Samples were stored in benchtop desiccators without controlling for exposure to oxygen.

### Ambient conditions scanning tunneling microscopy

Scanning tunneling microscopy measurements were performed with a custom-built Besocke-style with a platinum/iridium tip (80:20) in constant current mode under ambient conditions.<sup>S3</sup> Samples were held at a fixed bias as noted in figure captions. The known lattice of the 1-decanethiolate SAMs on Au{111} was used for calibration. STM images were analyzed using MATLAB (Mathworks, Natick, MA) and Gwyddion (<http://gwyddion.net/>).

### Low-temperature, ultrahigh vacuum scanning tunneling microscopy

MXene samples were vacuum sealed and shipped before being loaded into the vacuum chamber for STM investigation. The MXene sample was resistively heated at  $\sim 490$  °C in ultrahigh vacuum until the sample was fully outgassed, using an SiC wafer as the underlying substrate heater, to remove adsorbed water and any surface contaminants.

Heater temperatures were calibrated with a NiCr-NiAl type K thermocouple before sample annealing.

Low-temperature measurements were performed with a Createc GmbH scanning probe microscope operating under ultrahigh vacuum (pressure  $< 2 \times 10^{-10}$  mbar) at liquid helium temperatures ( $T < 6$  K). Etched tungsten tips were used during acquisition. Tip apexes were further shaped by indentations onto a gold substrate for subsequent measurements taken over MXene coated substrates. STM images are taken in constant-current mode with a bias applied to the sample. STS measurements were recorded using a lock-in amplifier with a resonance frequency of 683 Hz and modulation amplitude of 5 mV. Hyperspectral STS were recorded with gpSTS, which is a library for autonomous STS experimentation.<sup>S5</sup>

#### Atomic force microscopy

Atomic force microscopy images were recorded with a Bruker Dimension Icon microscope under ambient conditions, operating in Tapping Mode and using TESPA-V2 tips with spring constant,  $k = 42$  N/m. Images were captured at scan rate of 1 Hz with 1024 lines per image.



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## AUTHOR CONTRIBUTIONS

Conceptualization, K.E.W., Y.Z.C., S.I., J.C.T., K.C.L., Y.G., and P.S.W.; Materials synthesis, S.I.; Recorded and analyzed the scanning probe images and spectra, K.E.W., G.G, K.B., J.C.T., and A.W.-B.; Theory and calculations, Y.Z.C. and K.C.L.; Original draft, writing, reviewing, and editing, all authors. Funding acquisition, A.W.-B., K.C.L., Y.G., and P.S.W.; Resources, A.W.-B., K.C.L., Y.G., and P.S.W.; Supervision, A.W.-B., K.C.L., Y.G., and P.S.W.

## DECLARATION OF INTERESTS

The authors declare no conflicts of interest.

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## FIGURE CAPTIONS

**Figure 1.** **a)** Optimized structure of ternary mixed  $\text{Ti}_3\text{C}_2\text{T}_x$  where  $x$  is =O, -OH, and -F. **b)** Side view of the optimized  $\text{Ti}_3\text{C}_2\text{T}_x$  structure on gold. **c)** Optical microscopy image of single-layer flakes of  $\text{Ti}_3\text{C}_2\text{T}_x$  on silicon. **d)** Atomic force microscopy image of a single  $\text{Ti}_3\text{C}_2\text{T}_x$  flake showing small, oxidized regions (white dots) around flake edges and on the exposed top surface.

**Figure 2.** **(a-d)** Scanning tunneling microscopy (STM) images at various resolutions showing surface details, as well as **(e, f)** local scanning tunneling spectroscopy (STS), current-voltage ( $I$ - $V$ ) electronic spectra, of  $\text{Ti}_3\text{C}_2\text{T}_x$ . **a)** Ambient condition STM image ( $T = 298$  K). **b-d)** Low temperature ( $T = 4$  K), ultrahigh vacuum STM images. Inset in **(c)** shows the related fast Fourier transform with distorted hexagonal symmetry and a nearest neighbor distance of 1.1 nm. **e)**  $I$ - $V$  and **f)** differential conductance,  $dI/dV$ , spectra measured on the positions shown by the red triangles in **(d)**. Red traces represent individual and black represent averaged spectra. Raw scan data are shown in the Supplemental information (**Figures S3-S24**).

**Figure 3.** **a)** Calculated electronic density of states of  $\text{Ti}_3\text{C}_2\text{T}_x$  with mixed surface terminations on Au. The Fermi level,  $E_F$  is set as zero at the energies scale. Insets show

the surface adatom distribution with color codes: red-O, green-F, and blue-OH. **b)** Calculated electronic ( $I$ - $V$ ) spectra of ternary mixed terminated  $\text{Ti}_3\text{C}_2\text{T}_x$  on Au with changing compositions of  $\text{T}_x$ . **c)** Calculated differential conductance ( $dI/dV$ ) spectra of the same compositions shown in **(b)**.

**Figure 4. a)** Ultrahigh vacuum STM image ( $I_{\text{tunnel}} = 30 \text{ pA}$ ,  $V_{\text{sample}} = 1.0 \text{ V}$ ). Red and black markers show locations where the red and black tunneling ( $I$ - $V$  and  $dI/dV$ ) spectra were recorded, respectively. **b)** Tunneling  $I$ - $V$  spectra collected from the locations in **(a)**. **c)** Differential conductance ( $dI/dV$ ) spectra recorded at the locations indicated in **(a)**. Vertical lines mark the locations of -10 and +10 mV sample bias voltage peaks. **d, e)** Differential conductance maps of the  $2.5 \text{ nm} \times 2.5 \text{ nm}$  area indicated in the dashed white box in **(a)**, recorded at sample bias voltages of **d)** -10 mV and **e)** +10 mV.

**Figure 5. a)** Ultrahigh vacuum STM image reproduced from **Figure 2c**. The green line (7.3 nm) marks the location of the line scan of the differential conductance ( $dI/dV$ ) spectra shown in **(b)**. **b)** Heat map of the  $dI/dV$  spectra taken at each point along the green line, indicating the opening of a band gap. Data have been normalized from -1 to 1 using the maximum of each individual scan for better comparison of band gaps. **c)** Calculated  $dI/dV$  spectra across a mixed terminated OH-rich  $\text{Ti}_3\text{C}_2\text{T}_x$  surface (blue) and  $\text{Ti}_3\text{C}_2\text{T}_x$  with

a TiO<sub>2</sub> cluster on the surface shown in inset (orange). Raw scan data are shown in the Supplemental information (**Figures S27-S64**).











