

pH, Nanosheet Concentration, and Antioxidant Affect the Oxidation of $Ti_3C_2T_x$ and Ti_2CT_x MXene Dispersions

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The chemical stability of 2D MXene nanosheets in aqueous dispersions must be maintained to foster their widespread application. MXene nanosheets react with water, which results in the degradation of their 2D structure into oxides and carbon residues. The latter detrimentally restricts the shelf life of MXene dispersions and devices. However, the mechanism of MXene degradation in aqueous environment has yet to be fully understood. In this work, the oxidation kinetics is investigated of $Ti_3C_2T_x$ and Ti_2CT_x in aqueous media as a function of initial pH values, ionic strengths, and nanosheet concentrations. The pH value of the dispersion is found to change with time as a result of MXene oxidation. Specifically, MXene oxidation is accelerated in basic media by their reaction with hydroxyl anions. It is also demonstrated that oxidation kinetics are strongly dependent on nanosheet dispersion concentration, in which oxidation is accelerated for lower MXene concentrations. Ionic strength does not strongly affect MXene oxidation. The authors also report that citric acid acts as an effective antioxidant and mitigates the oxidation of both Ti₃C₂T_y and Ti₂CT_y MXenes. Reactive molecular dynamic simulations suggest that citric acid associates with the nanosheet edge to hinder the initiation of oxidation.

1. Introduction

MXenes are a family of transition metal carbides, carbonitrides, and nitrides with layered 2D nanostructures and have a general formula $M_{n+1}X_nT_x$, where M represents an early transition metal element such as titanium (Ti), vanadium (V), and niobium (Nb), X is carbon and/or nitrogen, T refers to one or multiple terminal

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groups (–OH, =O, –F), *n* usually ranges from 1 to 3, and *x* reflects the number of terminal groups.^[1–5] MXenes have drawn much attention for their potential use in energy storage,^[1,6] sensing technology,^[7,8] functional coatings,^[9–11] plasmonics,^[12] and catalytic applications^[13–15] due to their high electrical conductivity, hydrophilicity, and surface charge. Most of those properties can be traced back to their metallic-like 2D structure and functional groups attached during the etching and delamination processes.^[4,5,16–18]

However, recent studies suggest that MXenes are prone to react with dissolved oxygen and water molecules, which results in the formation of transition metal oxides and carbon residues.^[3,19,20] Initially, Zhang et al. claimed that MXene oxidizes due to the contact with dissolved oxygen in water.^[20] However, Huang et al. and our group also demonstrated that water molecules, rather than oxygen molecules, play a critical role in

MXene degradation.^[21,22] MXenes were reported to oxidize and degrade more rapidly in water rather than in organic solvents, air, or polymer matrixes.^[3,23] Zhang et al., Chae et al., and Habib et al. (our group) also found that temperature and humidity have an influence on MXene oxidation.^[3,19,20] They proposed that low temperatures and low humidity can mitigate the oxidation of MXene nanosheets due to the slower reaction kinetics and reduced exposure to water molecules, respectively. In addition, MXene nanosheets that are single- to few-layered or have smaller lateral size oxidize faster than multilayered MXene clay particles or larger-size nanosheets. MXenes oxidize rapidly when exposed to oxidizers such as hydrogen peroxide or treated by flash-annealing at high temperatures.^[24,25] In addition, elemental composition may influence the oxidation kinetics.^[26] VahidMohammadi et al. and Huang et al. reported that M2XTx MXenes, such as V_2CT_x and Ti_2CT_x , oxidize and degrade much faster than the more common $M_3X_2T_x$, such as $Ti_3C_2T_x$.^[21,27] Other aspects may also contribute to the oxidation of MXenes, such as the amount and types of terminal groups, etching conditions, ultraviolet exposure, and the number of defects on the MXene nanosheets.[3,28,29]







Figure 1. a) Schematic, and b,c) results for $Ti_3C_2T_x$ and Ti_2CT_x MXene nanosheet oxidation in aqueous dispersions with acidic and alkaline pH. A chemical structure of $Ti_3C_2(OH)$ is used in the schematics.

The shortened shelf life of MXenes due to their oxidation and degradation, has prompted a search for strategies to prevent or mitigate their oxidation and degradation. Wu et al. developed a carbon nanoplating technique to inhibit oxygen exposure and transport on the surface of $Ti_3C_2T_x$ MXenes.^[30] Our group and Natu et al. discovered that some antioxidants (such as sodium L-ascorbate) and polyanions (such as polyphosphates) slow the oxidation of $Ti_3C_2T_x$ and extend significantly their shelf-life.^[22,31] Shuck et al. reported that $Ti_3C_2T_x$ MXenes derived from MAX phase made from graphite as the carbon source are more stable than that from lampblack and titanium carbide (TiC).^[32] However, so far, these studies are limited to $Ti_3C_2T_x$ and have not been applied to any M_2XT_x MXenes.^[22,31]

Here, we investigate the oxidation kinetics of both $Ti_3C_2T_x$ and Ti_2CT_x nanosheets in acid, base, and buffer-adjusted dispersions over a pH range varying from 2 to 10 to elucidate oxidation mechanism in aqueous dispersions. The study aims at how both (i) oxidation affects the pH value of the MXene dispersion and (ii) pH affects the oxidation rate. These relationships markedly differ for $Ti_3C_2T_x$ and Ti_2CT_x . In addition, buffers with different pH are used to separate these inter-related effects from one another by artificially keeping pH constant over time. Even nanosheet concentration can affect oxidation rates, likely due to intersheet interactions and steric shielding. In the case of the buffer-adjusted dispersion study, we also discovered an effective antioxidant, citric acid, which mitigates the oxidation of both $Ti_3C_2T_x$ and Ti_2CT_x . In our study, the degree of oxidation of MXenes is mainly evaluated by X-ray photoelectron spectroscopy (XPS) and electrical conductivity changes of dried films made by vacuum filtering the aqueous MXene dispersions exposed to oxidation. Colloidal property changes are examined through ζ -potential and dynamic light scattering measurements. Reactive molecular dynamics (ReaxFF)^[33] simulations are also used to evaluate the oxidation stability of $Ti_3C_2T_x$ nanosheets in acidic and basic systems, and in the presence of citric acid.

2. Results and Discussion

Titanium carbides $Ti_3C_2T_x$ and Ti_2CT_x are used in this study as the most-studied members of MXenes family. The etching, delamination, and dispersion processes follow the prior works.^[3,22] The as-prepared MXene dispersions were first diluted to a concentration of 0.3 mg mL⁻¹. To evaluate the oxidation rate of MXene nanosheets in various pH conditions, the MXene nanosheet dispersions were adjusted to desired pH values by adding 0.1 m potassium hydroxide (KOH) or 0.1 m hydrochloride acid (HCl) solutions as illustrated schematically in **Figure 1**a. Here we also provide a roadmap of the study on the oxidation







Figure 2. a) The pH of $Ti_3C_2T_x$ MXene aqueous dispersions changes with time; b) the atomic percentage changes for Ti(IV) component obtained by X-ray photoelectron spectroscopy for $Ti_3C_2T_x$.

stability of $Ti_3C_2T_x$ and Ti_2CT_x in dispersions with different initial pH, displayed in Figure 1b,c.

2.1. $Ti_3C_2T_x$ Oxidation and pH

The drifts in the pH value of the $Ti_3C_2T_x$ MXene aqueous dispersions were recorded and reported in **Figure 2**a for dispersions with varying initial pH values. Rapid decreases in the pH values were observed in the first two days for two initially alkaline dispersions, followed by gradual decreases in pH value. The initially dramatic decreases in pH for the alkaline dispersions are likely due to the rapid uptake of hydroxyl ions. A reference dispersion for which the initial pH was not adjusted (natural pH = 4.4) only slightly decreased with time.

The chemical composition changes of $Ti_3C_2T_r$ nanosheets were monitored using XPS, shown in Figure S1 in the Supporting Information. The atomic percentage of Ti(IV), as an indicative of TiO₂ content formed due to oxidation, was obtained by analyzing the high-resolution Ti 2p spectra. Examples of spectra deconvolution and fittings for MXene samples with various degrees of oxidation are displayed in Figure S2 in the Supporting Information. It is clear in Figure 2b that the initially alkaline $Ti_3C_2T_x$ dispersions show a higher atomic percentage of Ti(IV) component than the initially acidic dispersion, which indicates a faster transition from MXene nanosheets to TiO₂ in alkaline media. Oxidation of MXene nanosheets in acid-adjusted dispersions was similar to the reference dispersion at pH = 4.4. We also observed that the nanosheets in dispersion with initial pH of 2.6 oxidized slightly faster than that in dispersion with initial pH of 3.6. The reason behind this is still not clear and is subject of our further investigation. It is possible that there is some defect formation caused by the MXene surface reacting with a strong acid. This confirms that alkaline conditions promote oxidation of MXene nanosheets in aqueous media.

The colloidal stability of $Ti_3C_2T_x$ MXene dispersions with a specified initial pH was evaluated by characterizing ζ potential over time (shown in **Figure 3**a). In the first two days, ζ potential became more positive rapidly for both acidic and basic media MXene dispersions; this can be explained by the adsorption of H⁺ and K⁺ cations onto the electronegative basal plane of the

MXene nanosheets. However, the alkaline dispersions exhibit a relatively slower increase of ζ potential over the 40 days, likely due to induced repulsion from the -O⁻ groups.

Oxidation may also cause the ζ potential value to become more positive. During storage, MXene nanosheets gradually lose colloidal stability due to conversion to TiO₂.^[22,31,34] For initially acidic media, MXenes colloid stability declines with time, as indicated by the increasingly more positive ζ potential values and the drastic increase in the hydrodynamic size (shown in Figure 3b). Note that this aggregation of the MXene nanosheets in acidic dispersions may contribute to the slower oxidation rate due to the smaller surface to volume ratio.

The electrical conductivity was measured for vacuum filtered films made from MXene dispersions that had been stored in dispersions with different initial pH for varying times. It has been previously determined that the oxidation of MXenes is correlated with the diminishing electrical conductivity.^[3,19,22,34] Figure 3c confirms that the fast oxidation of Ti₃C₂T_x in alkali environments is correlated with related decreases in the conductivity of Ti₃C₂T_x films. For nanosheets in dispersion with an initial pH of 10.3, the conductivity of the assembled film dropped from 1.6 ± 0.78 × 10⁵ S m⁻¹ to 4.1 ± 0.1 × 10⁴ S m⁻¹ in 18 d and dropped below the measurable limit of 10⁻⁶ S m⁻¹ in 30 d.

The downward pH drifts of MXene dispersions with initially alkaline pH values indicate that the majority of hydroxyl ions introduced from the added KOH are consumed within the first two days. On the MXene nanosheet basal plane, OH⁻ ions react with the protons disassociated from the –OH terminal groups. As a result, the –OH terminal groups are deprotonated to $-O^{-,33}$ displayed in the reaction below.

$$\mathrm{Ti}_{n+1}\mathrm{C}_{n}\mathrm{OH} + \mathrm{OH}^{-} \to \mathrm{Ti}_{n+1}\mathrm{C}_{n}\mathrm{O}^{-} + \mathrm{H}_{2}\mathrm{O}$$
(1)

Additionally, the pH drift may also stem from negatively charged OH⁻ ions associating with positively charged nanosheet edges.^[34] A counter-hypothesis (from Huang et al.) is that acidic carbon derivatives, such as carbonic acid or carbonates, may form because of degradation of MXene nanosheets.^[21] However, we argue that the formation of acidic carbon derivatives may not be the reason for the rapid pH decrease because





Figure 3. a) ζ potential and b) hydrodynamic diameter changes for Ti₃C₂T_x dispersions (initial pH indicated in the legend) over the course of 40 d. Dispersions were diluted to ~0.01 mg mL⁻¹ for ζ potential and size measurements; c) electrical conductivity of vacuum-filtered films made from Ti₃C₂T_x MXene dispersions of varying ages; conductivity of the film made from an initial pH 10.3 Ti₃C₂T_x dispersion dropped below ~10⁻³ at day 30 measurement (not shown).

the increased presence of Ti(IV) in $Ti_3C_2T_x$ is not proportional to the rapid pH drop.

Our findings above suggest that the hydroxyl anions play an important role in the oxidation of colloidal MXene nanosheets. Two separate mechanisms may be occurring in alkaline conditions.



The hydroxyl anions play an important role in the deprotonation of -OH terminal groups on MXenes sheets, resulting in the less-stable $-O^-$ groups. We speculate that the deprotonated $-O^{-}$ groups render the MXene surface more reactive, which leads to faster oxidation. In addition, the OH- from the base may be uptaken by and react with the relatively positive-charged MXene sheet edges resulting in degradation. These findings imply that MXene processing and utilization in basic environments, such as in TMAOH, TBAOH, and NaOH, may lead to suboptimal or declining performance due to oxidation. Specifically, this result suggests that alkaline supercapacitor electrolytes might degrade MXene electrodes over time. As for acidic conditions, MXene sheets have slower oxidation rates indicating an oxidation mechanism similar to the MXene sheets without pH adjustments. The more active MXene edges may first react with OH⁻ and H₂O. For edge-on degradation, the sheets then become smaller in size and gradually oxidize. In addition, introducing strong acids may cause defect formation, resulting in more reactive spots and a slightly higher oxidation rate

To study the effect of continuously supplying hydroxyl anions on MXene oxidation, $Ti_3C_2T_x$ nanosheets were dispersed in various buffer solutions and their oxidation stability was evaluated. **Figure 4**a shows that the pH of the buffered MXene dispersions barely changes (in contrast to unbuffered analogs in Figure 2a). The films produced from buffered alkaline dispersions indicate more rapid formations of TiO_2 (shown in Figure 4b and Figure S3 (Supporting Information)) than the alkaline dispersions with specified initial pH values. Consistent with this finding, the electrical conductivity of vacuum-filtered MXene films created from the buffered alkaline dispersions (Figure 4c) shows faster declines. We conclude that the alkaline buffers accelerate MXene oxidation to a greater extent because of the higher amount or "nearly unlimited" supply of hydroxyl anions.

In order to rule out any possible side effects brought by the salt ions in the commercial buffer solutions as we evaluated the role of OH⁻ and H⁺ ions, we further investigated the oxidation kinetics of Ti₃C₂T_x nanosheets in dispersions periodically supplied with 0.1 \times KOH or HCl to maintain relatively constant pH values (shown in **Figure 5**). Both the increase in TiO₂ formation and the rapid conductivity decline of subsequently vacuum-filtered films indicate that Ti₃C₂T_x oxidizes rapidly when hydroxyl ions are supplied continuously. In contrast, vacuum-filtered films produced from the acidic dispersions showed a fairly stable electrical conductivity (≈4.0 × 10⁵ S m⁻¹ over the course of 18 d).

In addition, we examined the oxidation of $Ti_3C_2T_x$ nanosheets in sodium chloride and potassium chloride solution with an ionic strength of 0.1 M. The similarities in the degree of oxidation to the reference dispersion without any added salt (indicated by the similar TiO₂ percentages shown in Figure S4 in the Supporting Information) suggest that the addition of salt ions, such as K⁺ and Cl⁻, has minimal effect on MXene oxidation. However, the addition of salt can disrupt the colloidal stability of MXene dispersions because of the reduced Debye screening length. Observed agglomerates of MXene nanosheets precipitated and settled down entirely within only a few hours in 0.1 m KCl.

We also discovered that oxidation stabilities are different for $Ti_3C_2T_x$ nanosheets derived from the Ti_3AlC_2 MAX phases with and without Ti_2AlC impurities. The Ti_2AlC phase, considered as







Figure 4. a) pH values change over time for the $Ti_3C_2T_x$ nanosheet buffer dispersions; b) the atomic percentage changes for the Ti(IV) component obtained by X-ray photoelectron spectroscopy for $Ti_3C_2T_x$; c) electrical conductivity of vacuum-filtered films made from $Ti_3C_2T_x$ MXene in buffer solutions of varying ages. Each sample was maintained at a specified pH in buffer solutions. The dispersions in the study were kept at a concentration of 0.3 mg mL⁻¹.

an impurity phase here, was indicated by (002) plane detected using X-ray diffraction, as shown in Figure S5a in the Supporting Information. From Figure S5b,c in the Supporting Information, X-ray photoelectron spectroscopy suggests that nanosheets derived from the Ti₃AlC₂ MAX phase with Ti₂AlC impurities bear much faster oxidation. This may result from defects on Ti₃C₂T_x nanosheet resulting from the degraded Ti₂CT_x grains. These defects may provide more edges for initializing oxidation.

2.2. Ti₂CT_x Oxidation and pH

We also investigated the effects of initial pH of aqueous dispersion on the oxidation stability of Ti₂CT_x nanosheets. At high pH, the pH drift for the Ti_2CT_r dispersions exhibited trends similar to that of $Ti_3C_2T_x$, shown in Figure 6a. However, for the Ti₂CT_x dispersion, its pH value declined far more rapidly due to the swift Ti_2CT_x oxidation as compared to $Ti_3C_2T_x$. On the other hand, initially acidic dispersions maintained relatively stable pH values over time for both Ti₂CT_r and previously studied $Ti_3C_2T_x$ dispersions. The chemical composition changes of Ti₂CT_x nanosheets were monitored by XPS, shown in Figure 6b. Unlike the more rapid increase in the atomic percentage of Ti(IV) component in initially alkaline dispersions for $Ti_3C_2T_{r_2}$ oxidation is uniformly rapid in both alkaline and acidic environments for Ti₂CT_x. In addition, more rapid drops of electrical conductivities are observed for Ti₂CT_{x2} as shown in Figure 6c. Films made from Ti₂CT_x dispersions generally lost their conductivity much faster (dropping below 10⁻⁶ S m⁻¹ in 6 h) than films made by $Ti_3C_2T_x$.

The oxidation stability of Ti_2CT_x nanosheets were also evaluated in various buffer solutions, shown in **Figure 7**. It is interesting to see that the oxidation is initially fast in the alkaline buffer (pH = 10.0); however, in the later stage of observation, the Ti(IV) percentages become highest for Ti_2CT_x dispersed in the water and in the acetate buffer (pH = 3.25).

2.3. Concentration Effects on Oxidation

In a separate study, we found that oxidation kinetics of MXene nanosheets depend heavily on the colloidal concentration. $Ti_3C_2T_x$ dispersions with five different concentrations were examined periodically for the signs of oxidation. Figure 8 suggests that $Ti_3C_2T_r$ oxidizes much faster in dilute dispersions as compared to higher concentrations, as indicated by (i) the accelerated formation of TiO₂ and (ii) the decline in the electrical conductivity of the vacuum-filtered film. The reason for the slow kinetics of MXene oxidation in high-concentration dispersions can be attributed to the capping and steric shielding effects among MXene nanosheets in close proximity; this restricts water's access to the MXene sheet edges, where oxidation initiates. The relevant concentrations can be estimated by considering an individual nanosheet as a circular disk with a diameter of *D* and a thickness of *t*. The semidilute transition volume fraction φ^* for any anisotropic disc can be determined from the ratio of the disc volume to the volume that the disc sweeps out during rotational Brownian motion, expressed as



Figure 5. a) Observed pH for $Ti_3C_2T_x$ dispersions with time; the pH of the dispersion was adjusted periodically to a desired value by supplying extra KOH or HCl; b) conductivity of films made from $Ti_3C_2T_x$ dispersions described in panel (a); c) atomic percentages for the Ti(IV) component obtained by X-ray photoelectron spectroscopy for $Ti_3C_2T_x$ films prepared from the dispersions described in (a).





Figure 6. a) The pH of Ti_2CT_x MXene dispersions changes with time; b) the atomic percentage changes for Ti(IV) component obtained by X-ray photoelectron spectroscopy for Ti_2CT_x ; c) electrical conductivity of vacuum-filtered films made from Ti_2CT_x MXene dispersions of varying ages; conductivities of Ti_2CT_x films made from the reference and acidic dispersions dropped below $\approx 10^{-3}$ in less than 10 h after being made (not shown).

$$\varphi^* = \frac{V_{\text{disc MXene}}}{V_{\text{sphere}}} = \frac{3t}{2D} \tag{2}$$

 $Ti_3C_2T_x$ MX enes have a density around 3.7 g cm⁻³;^[35] and the volume fraction can be related to concentration as

$$\varphi = \frac{c}{\rho_{\rm MXene}} \tag{3}$$

Based on images taken by atomic force microscopy (shown in Figure S6 in the Supporting Information), we assume that MXene nanosheets have an average lateral size of 1.5 μ m and an average thickness of 1.2 nm. The critical concentration (*c**) at which the nanosheets will start affecting each other can be estimated as 4.4 mg mL⁻¹ by

$$c^* = \rho_{\text{MXene}} \phi^* \tag{4}$$

This suggests that at dispersion concentrations higher than c^* , as in Figure 8a, the edge–edge interactions of nanosheets will prevent edge oxidation. Accordingly, the MXene dispersion having the highest concentration of 77 mg mL⁻¹ exhibited the least oxidation.

To further understand the role of particle-particle interactions (determined by nanosheet concentration) on oxidation, asprepared $Ti_3C_2T_x$ aqueous dispersion (3.6 mg mL⁻¹) and Ti_2CT_x aqueous dispersion (6.0 mg mL⁻¹) were stirred at 500 rpm for 20 d and 40 h respectively at room temperature in the dark. The stirred MXenes were severely oxidized. The atomic percentage of Ti(IV) increased dramatically from 6.0% to 35.9% for stirred $Ti_3C_2T_x$, as shown in Figure S7 in the Supporting Information. For stirred Ti_2CT_x , the Ti(IV) percentage increased dramatically from 9.7% to 78.9%, as shown in Figure S8 in the Supporting Information. In contrast, reference dispersions kept statically under the same conditions reached a final Ti(IV) percentage of 8.6% for Ti₃C₂T_x and 54.9% for Ti₂CT_x respectively. The agitation disrupts the particle–particle steric shielding leading to accelerated oxidation. This observation (stirring versus not stirring) confirms the idea of edge to edge interactions impacting oxidation.

2.4. Citric Acid Prevents Degradation of Ti₃C₂T_x and Ti₂CT_x MXenes

Interestingly, we discovered that a weak organic tricarboxylic acid-citric acid (CA), which is one of the components of the acidic buffer solution (pH = 3), is an effective antioxidant for protecting MXenes from oxidation and degradation. Both $Ti_{2}C_{2}T_{r}$ and $Ti_{2}CT_{r}$ MXene in this acidic buffer did not show much oxidation, as indicated by the relatively stable electrical conductivities and small changes in the Ti(IV) percentage shown in Figure 4 for $Ti_3C_2T_x$ and Figure 7 for Ti_2CT_x . Compared to the previously reported antioxidants such as a polyphosphate reported by Natu et al.[31] and L-ascorbate anion reported by our group,^[22] citric acid enables MXene nanosheets to have a much higher and longer stability in terms of chemical composition (shown in Figure 9 and Figure S9 (Supporting Information)). It is surprising to see from Figures 9a,b that the Ti(IV) percentage does not rise at all for Ti₃C₂T_r vacuum-filtered films made from nanosheets protected by citric acid after even five months and longer, while severe oxidation and nearly complete degradation were observed after just 50 d for Ti₃C₂T_x dispersed in a water-only reference system. In addition, citric acid can be



Figure 7. a) pH values change over time for the Ti_2CT_x nanosheet buffer dispersions; b) the atomic percentage changes for the Ti(IV) component obtained by X-ray photoelectron spectroscopy for Ti_2CT_x ; c) electrical conductivity of vacuum-filtered films made from Ti_2CT_x MXene in buffer solutions of varying ages. Each sample was maintained at a specified pH in buffer solutions. The dispersions in the study were kept at a concentration of 0.3 mg mL⁻¹.







Figure 8. Oxidation kinetics of $Ti_3C_2T_x$ changes for MXene dispersions of varying concentrations indicated by a) the increase of Ti(IV) atomic percentage obtained using X-ray photoelectron spectroscopy and b) the drop in electrical conductivity of vacuum-filtered films; c) the color of as-prepared MXene nanosheet dispersions and the same dispersions on the 27th day (from left to right: 7.7, 1, 0.1, 0.05, 0.005 mg mL⁻¹).

used to mitigate the oxidation of Ti_2CT_x , as shown in Figure 9c–e, which was not reported in prior studies. The later can enable the widespread applications of Ti_2CT_x , which have been limited because of their rapid oxidation. To further demonstrate the antioxidation performance of citric acid in the citric acid buffer (pH = 3.0), MXene nanosheets were stored in an acetate buffer with a similar pH of 3.25. We found that the acetate buffer (pH = 3.25) does not protect MXenes from oxidation like the buffer containing citric acid, as shown in Figures 4b and 7b. In both buffers, the MXene sheets tend to aggregate; hence, the aggregation of nanosheets is the not the main factor that accounts for the $Ti_3C_2T_x$ stabilization in the citric acid-containing buffer.

Similar to other antioxidants such as ascorbate and polyphosphate ions, it is reasonable to infer that citric acid protects MXene oxidation through edge capping and shielding. Interestingly, citric acid in the acidic buffer showed better protection for Ti_2CT_x than citric acid in its aqueous solution, indicated by the low Ti(IV) percentage presented. To gain a better understanding of this, the performance of citric acid as an antioxidant was examined in acidic and alkaline environments respectively. Figure S10 in the Supporting Information suggests that citric acid is not effective in MXene protection in alkaline environment, in which the citric acid molecules are deprotonated (citric acid is a tricarboxylic acid with three different values of pKa = 3.1, 4.7, and $6.4^{[36]}$). This can be explained by the

electrostatic repulsion between the deprotonated citric acid anions and the overall negatively charged MXene nanosheets, which prevents the anion from approaching the MXene basal surfaces and edges for protection. In acidic environments, the antioxidative effect may be achieved by shielding interactions between citric acid molecules and MXene edges as the repulsion barrier is removed, and citric acid molecules are able to approach the nanosheets. In addition, it may also be a result of the hydrogen bonding interactions between MXene functional groups and the protonated citric acid carboxylic groups.

2.5. ReaxFF Simulations

Visualizing and understanding how the dispersed nanosheets interact with ionic species is a task best suited to molecular simulations. To further elucidate the mechanism of how pH affects the oxidation stability of MXene, ReaxFF molecular simulations were performed to examine a single-layer $Ti_3C_2T_x$ MXene nanosheet (Figure S11a, Supporting Information) in systems with altered pH (acidic and alkaline). Three systems were examined: (i) $Ti_3C_2T_x$ nanosheet surrounded by water molecules, (ii) $Ti_3C_2T_x$ nanosheet surrounded by hydroxyl ions and water molecules, and (iii) $Ti_3C_2T_x$ MXene nanosheet surrounded with protons and water molecules (Figure S12, www.advancedsciencenews.com

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Figure 9. X-ray photoelectron spectroscopy (XPS) spectra of Ti 2p for $Ti_3C_2T_x$ vacuum filtered films that had been stored at a concentration of 0.3 mg mL⁻¹ a) after 50 d in water and b) after 5 months in 1.5 mg mL⁻¹ citric acid solution; Ti_2CT_x films stored at a concentration of 0.3 mg mL⁻¹ after 40 h in c) water, d) 1.5 mg mL⁻¹ citric acid, and e) EMD Millipore buffer (pH = 3, made up of citric acid, sodium hydroxide, hydrogen chloride); the buffer solution shows better performance in mitigating the oxidation of Ti_2CT_x due to the interaction between citric acid molecules and nanosheets indicated by the high content of COO⁻ component (COO⁻ % = 32.5%) shown in f) the C 1s spectrum for MXene that had been stored in buffer solution.

Supporting Information). In Addition, a fourth system with a MXene nanosheet surrounded by water and citric acid molecules (Figure S13, Supporting Information) was also evaluated to examine the improved stability of nanosheets in the presence of this antioxidant. ReaxFF simulations were carried out at 500 °C for 25 ps using large-scale atomic/molecular massively parallel simulator (LAMMPS)^[37] and using the ReaxFF force field from Osti et al.^[38] To accelerate the kinetics of the reactions, simulations were carried out at a higher temperature as compared to the experiments, which is a common method.^[39]

In order to quantify the stability of the $Ti_3C_2T_x$ structures after oxidation, radial distribution functions (rdf) were computed for the Ti–C atoms for the last 2.5 ps of each simulation.

Only the carbon atoms in the MXene structure were considered for the rdf calculations. The radial distribution function, g(r), provides the probability of finding a particle at a distance r from another particle in 3D space. Our results indicate substantially less oxidation in the acidic system as compared to the basic system shown in **Figure 10**. A peak at 2.1 Å is observed in the Ti–C bond (the backbone of MXene structure) rdf calculations, which is characteristic of a crystalline $Ti_3C_2T_x$ structure. The rdf peak intensity at 2.1 Å for the acidic system is the highest, followed by the system with just water, and then the basic system. These simulations support the experimental measurements, as the Ti(IV) percentage of MXene stored in basic medium increases more rapidly as compared to acidic systems due to







Figure 10. Final molecular configuration of $Ti_3C_2T_x$ nanosheet after 25 ps ReaxFF molecular dynamic simulation of systems with a) $Ti_3C_2T_x$ MXene nanosheet, water, and protons (acidic environment), and b) $Ti_3C_2T_x$ MXene nanosheet, water, and hydroxyl ions (alkaline environment). c) The radial distribution functions of Ti–C bonds obtained by ReaxFF are shown for acidic, alkaline, and water-only systems. A higher peak intensity at 2.1 Å was obtained for nanosheets stored in the acidic system, suggesting a higher level of stability against oxidation.

oxidation in the presence of hydroxyl anions. The final frames of the oxidation simulations in acidic and basic systems are shown in Figure S14 in the Supporting Information.

To understand the mechanism driving the higher stability in acidic systems as compared to basic systems, we carried out a frame-by-frame examination of the simulation trajectories. As detailed in our previous publication,^[22] oxidation starts along the nanosheet edges in the system with only water and the $Ti_3C_2T_r$ nanosheet. For the acidic system, we observe that protons interact with water molecules to form H₃O⁺ intermediate species. These intermediate species as well as the MXene nanosheet edges are positively charged, therefore we observe minimal oxidation in the acidic system (Figure 10a). The MXene nanosheet stored in the basic system is primarily attacked by the highly reactive hydroxyl anions, with oxidation starting from the edges, and later affecting the basal plane as well (Figure 10b). The simulation results indicate that the MXene nanosheet stored in the basic system loses Ti atoms in the form of TiO₂ and other complex species with Ti, O, and H atoms. Overall, MXene stored in basic system show much faster oxidation due to the aggressive nature of hydroxyl ions.

Simulations of the effect of citric acid on the oxidation stability of MXene nanosheets show improved stability, mainly due to the steric shielding effect of citric acid along the edges. The final structure of a $Ti_3C_2T_x$ MXene nanosheet after 25 ps is shown in Figure S15a in the Supporting Information. The rdf calculations show a higher peak intensity at 2.1 Å as compared to just water and MXene system, suggesting less oxidation in the presence of citric acid (Figure S15b, Supporting Information).

3. Conclusions

Our study demonstrates that the oxidation kinetics of $Ti_3C_2T_x$ and Ti_2CT_x MXenes are dependent on the pH and concentration of the dispersions. MXene nanosheets in the aqueous phase can interact with hydroxyl anions rapidly, then become more prone to oxidation due to the unstable terminal group $-O^{-}$. Meanwhile, the pH value drops rapidly in the initially alkaline MXene dispersion. Hence, MXene processing and applications in alkaline environments may lead to suboptimal or declining performance due to the rapid oxidation. The oxidation of MXene nanosheets in various buffers were also examined, and the results suggest that the highest oxidation rate occurs when hydroxyl anions are continuously available. In addition, an effective antioxidant, citric acid, was discovered, which can effectively prevent or mitigate the oxidation of both "312" $Ti_3C_2T_x$ and "211" Ti_2CT_x . We also demonstrated that the oxidation rate decreases when the MXene dispersion concentration is high due to steric shielding effect among the nanosheets. With these new findings, we recommend that MXene dispersions be formulated to have a high concentration, acidic pH, and citric acid to minimize their oxidation.

4. Experimental Section

 $Ti_3C_2T_x$ MXene Nanosheet Preparation: The parent Ti_3AlC_2 phase was synthesized from the blends of Ti, Al, and graphite powders which were mixed at the ratio of 3.0:1.2:1.9 (Ti:Al:C). The bulk Ti₃AlC₂ was synthesized by heating up the powder mixture in a tube furnace to 1510 °C at 10 °C min⁻¹ and being kept for 4 h. The bulk Ti₃AlC₂ was grounded and sieved to the size below 45 μ m. Ti₃C₂T_x MXenes were prepared by the selective acid etching method described in the previous studies.^[17,32,40-42] Obtained multilayered $Ti_3C_2T_x$ clay was then intercalated and delaminated into nanosheets by sonication. The sonicated dispersion of nanosheets was then purified by centrifugation at 3600 rpm for 1 h to separate and remove the unexfoliated particles. Titanium-based MXene nanosheets were terminated with various functional groups during the acid etching and processing in aqueous phase such as hydroxyl group (-OH), atomic oxygen group (-O), chloride group (-Cl), and fluoride group (-F). These polar terminal groups grafted on the nanosheet surface endow the MXene nanosheets with strong hydrophilicity and electronegativity, which facilitates dispersion in an aqueous phase to form a relatively stable suspension. Note that in the concentration dependency study on MXene oxidation, to accelerate the experimental timescale, TiC was used as the carbon source in the MAX phase synthesis, which led to



faster oxidation kinetics for the nanosheets derived from that source. $^{\left[32\right] }$ The blends of Ti, Al, and TiC powders were mixed at a ratio of 1.2:1.2:1.8 (Ti:Al:TiC).

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 Ti_2CT_x MXene Sample Preparations: The parent Ti₂AlC MAX phase was synthesized from the blends of Ti, Al, and graphite powders which were mixed with 2.0:1.0:1.0 (Ti:Al:C) ratio. The bulk Ti₂AlC was synthesized by heating the powder mixture in a tube furnace to 1410 °C at 10 °C min⁻¹ and maintaining the temperature for 4 h. Synthesized bulk Ti₂AlC was grounded and sieved to the size below 20 μ m. Ti₂CT_x MXenes were prepared by the modified selective acid etching method similar to the Ti₃C₂T_x with reduced reaction time. Obtained multilayered Ti₂CT_x clay was then intercalated and delaminated into nanosheets by sonication. The sonicated dispersion was then purified by centrifugation at 3600 rpm for 1 h to separate and remove the unexfoliated particles.

Diluted and Dispersed MXene Sample Preparations: As-prepared MXene nanosheet dispersions were first diluted with water to 0.3 mg mL⁻¹ concentration. Then the pH values of the diluted dispersions were preadjusted to higher pH by addition of 0.1 M KOH solution, and to lower pH by addition of 0.1 м HCl, respectively. (The volumes of acid and base added are much smaller than the original volume of the MXene dispersion.) The starting pH values of the preadjusted Ti₃C₂T_v dispersion were kept at 10.3, 8.2, 3.6, and 2.6, respectively. The starting pH values of the preadjusted Ti_2CT_x dispersion were kept at 10.3, 8.4, 3.5, and 2.6, respectively. For the dispersed MXene nanosheets in buffers, as-prepared MXene dispersions were diluted directly into the concentration of 0.3 mg mL^{-1} using strong alkali buffer solution (pH = 10.00 at 25 °C, EMD Millipore, made up of boric acid/potassium chloride/sodium hydroxide), weak alkali buffer solution (pH = 8.00 at 25 °C, EMD Millipore, made up of boric acid/sodium hydroxide/hydrogen chloride), acidic acetate buffer solution (pH = 3.25 at 25 °C, made up of sodium acetate/acetic acid), acidic buffer solution (pH = 3.00 at 25 °C, EMD Millipore, made up of citric acid/sodium hydroxide/hydrogen chloride). In the concentrationdependent study, the as-prepared Ti₃C₂T_y MXene dispersion was diluted with water into concentrations of 7.7, 1, 0.1, 0.05, and 0.005 mg mL⁻¹. All samples were stored in sealed jars under dark conditions.

Materials Characterization: The pH values of the MXene dispersion samples were measured using a pH meter (Mettler Toledo, Switzerland). The surface chemical states of MXene nanosheets were studied using an Omicron XPS employing a Mg-sourced X-ray beam. The samples used for XPS analysis were prepared by vacuum filtering the stored MXene dispersions at each time of measurements. Before XPS analysis, the samples were dried under vacuum for two days to prevent possible outgassing. XPS accuracy should not be affected by the thickness (>100 nm) of these samples. XPS peak fittings and quantifications were analyzed using CasaXPS software (version 2.3.22). The high-resolution spectra and fittings of Ti 2p and C 1s are shown in Figure S2 in the Supporting Information. The fitted results of CH_x/C-O and O-C=O components in $Ti_3C_2T_x$ samples are summarized in Figure S16 in the Supporting Information. ζ potential and average hydrodynamic diameter changes of MXene dispersions were measured using a Zetasizer Nano ZS90 from Malvern Instruments, USA. Scanning electron microscope (SEM, JSM-7500F, JEOL, Japan) and atomic force microscope (AFM, Bruker, USA) were used to probe the morphology of dried MXene samples. The MAX and MXene morphologies obtained by SEM were shown in Figures S17 and S18 in the Supporting Information. X-ray diffraction (XRD) patterns were acquired using a Bruker D8 powder X-ray diffractometer with CuK α (λ : 1.5418 Å) radiation. X-ray patterns of MAX and MXene used in this study was shown in Figures S19, S20, and S21 in the Supporting Information. The electrical resistance or conductivity was measured using a four-point resistivity probe setup (Keithley Instruments, USA) on MXene films made by vacuum filtration. The thicknesses of the vacuum-filtered film used for conductivity measurements were almost same (1.17 \pm 0.05 $\mu m),$ measured for the cross-sections of each sample by SEM (shown in Figure S22 in the Supporting Information).

 $\it ReaxFF$ Simulation Setup: ReaxFF is a reactive force field MD simulation technique that uses the bond order concept to calculate the interaction between atoms at each time step.^[43] As compared

to other nonreactive atomistic simulations, a smooth transition between the nonbonded states and the bonded states is provided by ReaxFF. In ReaxFF, the total energy of the system can be summed up as follows

$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{lp}} + E_{\text{H-bond}}$ (5)

The total energy of the system (E_{system}) consists of bond-order dependent or covalent interactions and nonbonded interactions. Bond-order-dependent terms include the bond energy (E_{bond}), over-coordination (E_{over}), under-coordination (E_{under}), and hydrogen bond (E_{H-bond}) interactions. Energy penalty terms include torsion angle energy (E_{tor}), valence angle energy (E_{val}), and lone pair energy (E_{lp}), whereas the nonbonded interactions are van der Waals (E_{vdW}) and Coulomb energy ($E_{Coulomb}$). Interatomic distances are calculated and updated at every time step, and bond order is calculated between all pairs of atoms. Nonbonded interactions pairs. Quantum mechanics calculations typically optimize force field parameters describing energy terms. The force field used in this study has been fitted for Ti and C based MXene structures and has shown good correlation with experiments.^[22,38]

Four systems were generated for ReaxFF molecular dynamics simulations of MXene oxidation under different conditions. The first system had 200 water molecules and a single Ti₃C₂(OH) structure (Figure S11a, Supporting Information), and second and third systems had an additional 150 OH and H atoms, respectively. The fourth system had 200 water molecules, a single Ti₃C₂(OH) MXene nanosheet and 10 molecules of citric acid (C6H8O7) (Figure S11b, Supporting Information). The first three systems were evaluated to examine the effect of pH on the oxidation of MXene nanosheet, whereas the first and the fourth system revealed the improved oxidation stability of MXene in the presence of citric acid. The hydroxyl anions, protons, water molecules, and citric acid molecules were randomly distributed around the MXene structure. The density of all the systems was kept at \approx 1 g per cc. NVT simulations were carried out 500 °C (773 K) with 0.25 fs time-steps for a total time of 25 ps using LAMMPS.^[37] Simulations were carried at elevated temperatures as compared to the experiments to accelerate the kinetics of the reactions. rdf calculations were carried out using Visual Molecular Dynamics (VMD)^[44] for the last 2.5 ps of the oxidation simulations.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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Author Contributions

X.Z., J.L.T., M.R., and M.J.G. conceived the central ideas. X.Z. and J.W.B. carried out the design of experiments, material preparations, and characterization. A.V. performed the reactive molecular dynamics simulations. Z.T., D.H., and V.K. carried out the synthesis of the MAX particles. M.G., M.R., and J.L. overseen and directed the project. The manuscript was prepared by X.Z., A.V., and M.G. S.S. and T.H. aided in experimental design and interpretation. S.L. assisted with the DLS measurements. All authors provided comments on the data analysis and the manuscript writing.

Keywords

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