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ORIGINAL ARTICLE

Multi-year study of environmental stability of $Ti_3C_2T_x$ MXene films

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Abstract
MXenes are a family of two-dimensional (2D) carbides and nitrides with extraordinary electrical, optical, chemical, and electrochemical properties. There is a perception that MXenes are unstable and degrade quickly, limiting potential applications and requiring specific storage conditions to last for a long time. It primarily comes from studies on delaminated MXenes flakes in dilute dispersions and samples from defective or non-stoichiometric precursors when MXene research was in its infancy. In the years since then, significant developments in synthesis, processing, and understanding of their chemistry have led to dramatic increases in the environmental stability of many MXenes, especially the widely studied $Ti_3C_2T_x$. However, previous studies focused primarily on MXene dispersion, while in the majority of applications, MXenes are processed into films soon after synthesis. Herein, we analyze $Ti_3C_2T_x$ free-standing films aged from 4 to 10 years through structural and morphological characterization along with electrical conductivity measurements to reveal the effect, or lack thereof, of prolonged storage under ambient conditions. Further, we show that the decrease in electronic conductivity over time is caused mainly by water uptake by the hydrophilic surfaces of MXenes, which can be removed by vacuum annealing. As a result, the conductivity of the films can be partially or almost completely recovered.

Keywords MXene · Aging · Films · Stability · $Ti_3C_2T_x$

1 Introduction

MXenes, first reported in 2011, are a family of two-dimensional materials composed of alternating transition metals and carbon or nitrogen layers [1]. A diverse class of materials, they are known to have a wide range of applications in areas such as electromagnetic interference shielding [2], electrochemical energy storage [3], and gas- and bio-sensing [4], which utilize MXene films. Their environmental stability is one of the key requirements for industrial applications in those fields, as well as in printed and epidermal electronics, functional textiles, communication devices, and many other applications, where MXenes have shown promise and outperformed other materials [2–8].

The first discovered and most widely studied MXene is titanium carbide, $Ti_3C_2T_x$, produced by selective etching of Al from Ti_3AlC_2 MAX phase precursor [5]. Since 2011, the synthesis of $Ti_3C_2T_x$ has been extensively studied and optimized, leading to vastly improved physical and chemical properties, including stability of colloidal dispersions of MXene flakes in water surpassing a year, and electronic conductivity of free-standing MXene films over 20,000 S cm^{-1} [6]. Despite this, there is still a perception that MXenes degrade quickly, on the order of weeks or even days [7–9]. While this was true for a majority of MXenes at the early stages of MXene research and may still be a concern for specific M_2C MXene compositions, such as Ti_2CT_x and V_2CT_x, numerous strategies have since been developed to produce MXenes that remain stable for over a year in aqueous colloidal dispersions [10]. Improvements in the synthesis and processing of all MXene compositions are continually being made to reach the stability levels of $Ti_3C_2T_x$ MXene [11, 12].

Oxidation is the primary cause of MXene degradation over time [13]. Multiple factors affect oxidation rate, including MXene composition, form (powder, film, solution, etc.), and storage conditions [12]. The presence of water can lead to hydrolysis of MXene in solution [14] and accelerate oxidation through the exposure of the

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MXene interlayers. Through experimentation, it has been shown that when $Ti_3C_2T_x$ is in contact with water for a prolonged period, hydrolysis of the MXene layers assisted by the oxidizing effect of oxygen present in the water and air can facilitate $Ti_3C_2T_x$ conversion to titanium dioxide (TiO_2) [14, 15]. Oxidation can be quantified through conductivity measurements, as large conductivity drops have been shown by degradation of $Ti_3C_2T_x$ in air and when incorporated in solids such as polymers [16]. However, if the MXene is prepared in certain ways (M/C stoichiometry, large flakes, and low concentration of defects), the effects of oxidation and hydrolysis through interlayer water can be mitigated. Intercalation of organic molecules, such as *N*-methylformamide, between the MXene layers can also increase environmental stability [17].

Since as early as 2016, it has been known that drying at elevated temperatures can remove interlayer water from MXene films [18], and that removing water can enhance their conductivity [19] and environmental stability [20]. Vacuum drying can bypass potential oxidation due to the elevated temperature, but even drying $Ti_3C_2T_x$ in an oxygen-filled environment, such as ambient air, between 100 and 245 °C can improve conductivity by removing adsorbed and intercalated water and hydroxyl terminations without facilitating a decrease in its extinction coefficient or formation of TiO_2, which typically occurs above 450 °C [21].

One area of research that has developed rapidly in the past 5 years is the synthesis of the MAX phase precursors (for $Ti_3C_2T_x$, the MAX would be Ti_3AlC_2) [10, 22]. The properties of the MXene can vary significantly depending on the type of MAX used: for example, it was shown that MAX produced in three different ways (from graphite, carbon lampblack, and TiC) resulted in $Ti_3C_2T_x$ samples that varied in both conductivity and chemical stability [22]. In addition, the presence of aluminum exceeding the 3:1:2 stoichiometric ratios of Ti:Al:C during synthesis of the Ti_3AlC_2 MAX phase precursor resulted in superior crystallinity and carbon stoichiometry of the Ti_3AlC_2 [10]. MXenes produced with this MAX displayed improved stability, and free-standing films and aqueous suspensions resisted oxidation for over 10 months [10].

Another major change to improve the stability of the resulting MXene is to change the etching method of the MXene itself. In 2018, a combination of lithium fluoride (LiF) and hydrochloric acid (HCl) [23], which is significantly milder than the previously used 50 wt% hydrofluoric acid, became the most common etchant [24]. $Ti_3C_2T_x$ flakes synthesized in LiF/HCl (minimally invasive layer delamination or MILD method) demonstrated larger sizes and a lower concentration of point defects [23, 24]. Three etchants with 5 wt% HF were tested: pure HF, HF/HCl, and HF/H_2SO_4 [24]. These etchants yielded various surface terminations, affecting interlayer spacing and the amount of water present [24]. MXene etched in HF/H_2SO_4 had the cleanest surface with little to no sulfur, demonstrating the highest conductivity and the lowest amount of water [24]. However, the yield was lower than in the case of HF/HCl etching, so the currently established etchant for $Ti_3C_2T_x$ is a 6:3:1 ratio of HCl to deionized water to HF [10]. This 5 wt% HF, HF/HCl solution combined with advances in MAX phase synthesis yielded stable $Ti_3C_2T_x$ films that exhibited conductivity exceeding 20,000 S cm^{-1}, which changed only insignificantly over a year of storage [10].

At A.J. Drexel Nanomaterials Institute, there is convenient access to films made from the initial stage of MXene research in 2013, when the first delamination procedure was developed [25], to the present, which grants a unique opportunity to study MXene films aged over many years. Over the years, we developed techniques to characterize the quality of MXene films [26]. In this study, the conductivity of $Ti_3C_2T_x$ MXene films synthesized from 2014 onward was measured, and the samples that exhibited extremely high and very low conductivity were characterized. X-ray diffraction (XRD) and scanning electron microscopy (SEM) demonstrated that vacuum drying at the time of synthesis can retard degradation by removing interlayer water from the film. Drying, even after 5–10 years have passed, can still recover a significant amount of lost conductivity. Lastly, it was shown how synthesis and delamination methods to prepare the MXene films affect their conductivity and environmental stability over time.

2 Experimental methods

Film fabrication and collection. 65 free-standing films of $Ti_3C_2T_x$ MXene produced between 2014 and 2021 were collected for analysis. Films were produced through two deposition techniques: (1) vacuum-assisted filtration from colloidal dispersion of MXene in water through porous membranes (typically polyvinylidene difluoride (PVDF) with 450 nm pores) [27]; (2) spray coating from colloidal dispersion of MXene in water using a compressed air-backed spray gun onto Celgard membranes [28]. Of note, specific details regarding MAX and MXene synthesis, as well as preparation of individual films, varied over the years. However, the films were made using the best practices at the time.

Film storage. Most films were stored in folded weigh paper and inserted into sealable plastic bags. A few films were stored in plastic petri dishes.

Conductivity measurement of $Ti_3C_2T_x$ films. To acquire the conductivity of these films, the sheet resistance was measured using a Jandel four-point probe, and the thickness of the films was obtained using a Mitutoyo micrometer. In both cases, the measurements were taken at four points on the films and averaged.

Drying of $Ti_3C_2T_x$ films was done at 200 °C for 24 h in an Across International vacuum oven at less than 0.5 torr. After drying, the films were stored under a vacuum for 6 days before the XRD measurements were made.

X-ray diffraction analysis was performed using a Rigaku SmartLab diffractometer from 3 to 25° 2θ with a step size of 0.01°. The incident X-ray wavelength was 1.5406 Å (Cu Kα). For the pre-drying data, the scan rate was 1° per min, and for the post-drying data, it was 2° per min.

Scanning electron microscopy was performed using a Zeiss Supra 50 VP SEM. Samples were mounted on aluminum stubs using adhesive copper tape. Images were collected with an InLens detector at a working distance of 8–9 mm, a vacuum level of $1.5*10^{-5}$ Torr, and an accelerating voltage of 5.0 kV.

3 Results

Figure 1 summarizes conductivity measurements for the 65 films selected for this study. The wide range of conductivities of the measured $Ti_3C_2T_x$ films indicates a variety of synthesis methods, post-synthesis treatments, and storage conditions due to varying purposes and applications. Many of them resulted from the search for optimal synthesis conditions and had properties far from the best. Films with the best properties were typically used for various research purposes, from destructive characterization to device fabrication, and not left intact. Thus, conductivity measurements and conclusions about the stability of MXenes lean conservative, as there were likely samples from the same period that would perform better than the 65 selected film samples. Three films of note are labeled in Fig. 1a; of these, film "A" had the highest measured conductivity of all sample films in this study. With a conductivity of 9,750 S cm^{-1}, it

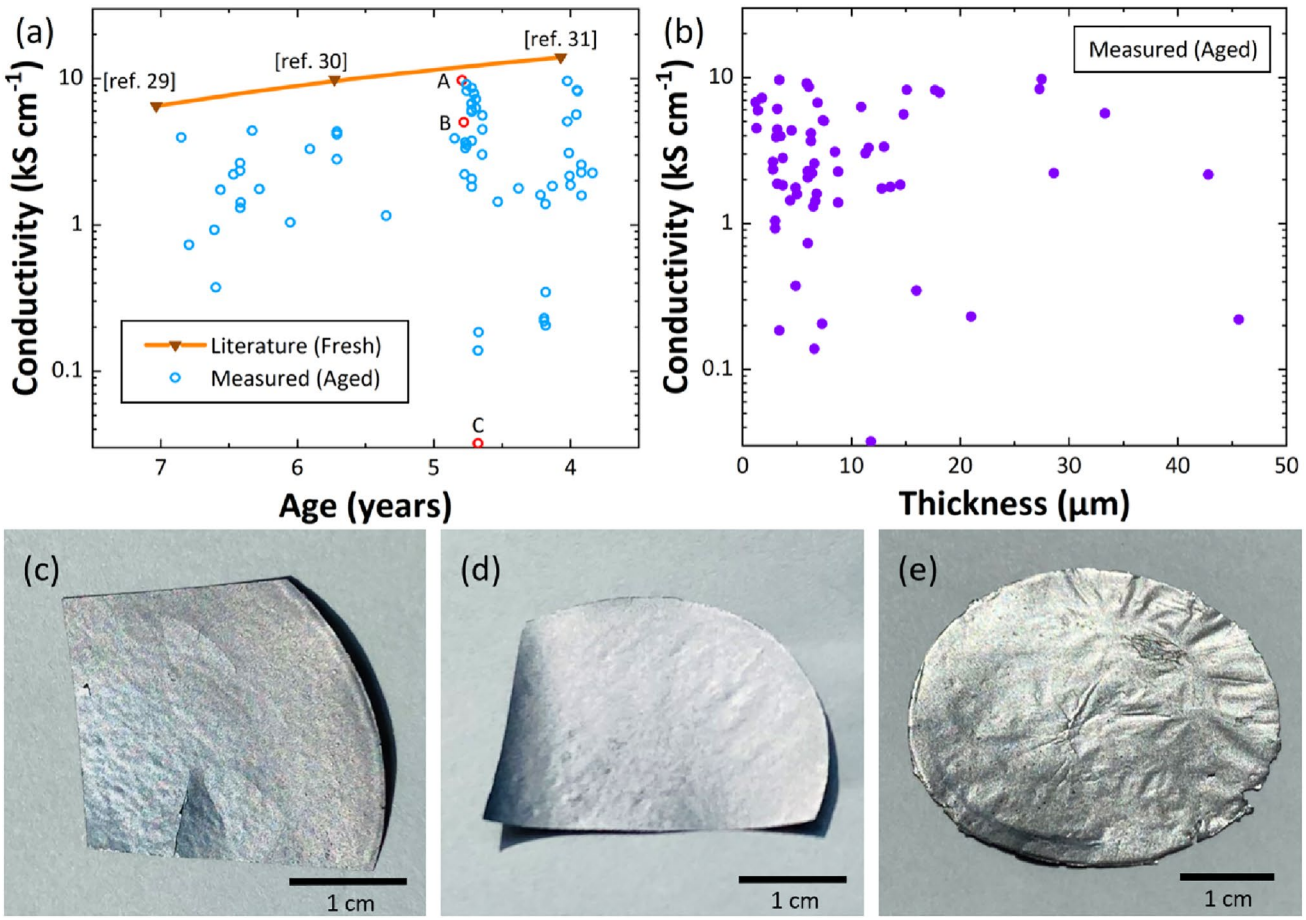

Fig. 1 **a** Measured conductivity of aged $Ti_3C_2T_x$ films compared with the maximum conductivity values from the literature [29–31] at the time of synthesis. Films of interest are colored red and discussed below. **b** The conductivity of the aged films plotted *vs.* film thickness. Photographs of selected films from Fig. 1a; from left to right, film A (**c**), film B (**d**), and film C (**e**). All three films kept their metallic luster and did not show visual signs of oxidation

compares favorably with the highest measured conductivities reported in the literature at the time of synthesis. Please note that the literature reports the conductivity of freshly prepared films, while film "A" studied here is after 5 years of storage. This film was marked with its measured sheet resistance and thickness, allowing for a direct comparison of its current measured conductivity to conductivity at the time of synthesis. Film A was dried at the time of synthesis at 200 °C for 24 h. In contrast, film "B", part of the same batch as A, was prepared similarly to A but was kept at room temperature after synthesis. Lastly, film "C" demonstrated the lowest conductivity of all films, at 32 S cm^{-1}. This film was delaminated with tetramethylammonium hydroxide (TMAOH). Optically, all films appeared metallic and shiny, with no visible degradation, and maintained good flexibility. Photographs of films "A", "B", and "C" are shown in Fig. 1c–e.

There is a clear difference between the conductivities of measured films greater than and less than 5 years old (Fig. 1a). Films greater than 5 years old did not exceed 5,000 S cm^{-1} (which is still an excellent value for the films aged 6–7 years), whereas the more recent films exhibited conductivities double that of the older films (Fig. S1). This steep increase in measured conductivity is likely due to the advances in MAX phase etching and MXene synthesis—the so known MILD method developed around that time, and the HF–HCl method used since 2021, which introduce less damage and produce higher quality MXene with a larger flake size and fewer point defects. In addition, the use of 5 wt% HF etching solution [24] not only yields MXenes with superior conductivity but also greater stability, allowing them to retain much higher conductivity over a prolonged time.

In Fig. 1b, conductivity is plotted *vs.* film thickness. Ideally, thickness should be inversely correlated with sheet resistance, resulting in an independent relationship between thickness and conductivity. However, as it is known that interlayer spacing can affect both conductivity and thickness, the correlation between conductivity and thickness was measured to determine whether it was necessary to adjust for thickness. The correlation value obtained was −0.018, close enough to zero that no adjustment was required. Thus, we can conclude that the film thickness did not affect the stability of MXene films and their properties after storage.

In addition to the information about the drying conditions, films A and B had conductivity data recorded at the time of synthesis, which allows for a comparison between the conductivities, shown in Fig. 2a (orange and green bars). Impressively, film A had a conductivity of 10,810 S cm^{-1} when synthesized and 9,750 S cm^{-1} when remeasured 5 years later—90% of its original value. In contrast, film B retained roughly 50% of its original conductivity. This discrepancy appears to be solely due to the drying of sample A at an elevated temperature, which shows the importance of the removal of interlayer water. To measure interlayer spacing, X-ray diffraction analysis was performed on films A, B, and C, as shown in Fig. 2b. Of note, film A exhibited a double peak at 7° and 9°, whereas film B had only a single peak at 7° 2θ. This indicates that film B's *d*-spacing is 12.6 Å throughout, whereas certain areas of film A have an interlayer spacing similar to film B, but other areas have a smaller *d*-spacing of 9.8 Å. The 2.8 Å difference is equivalent to the diameter of a single water molecule, so a monolayer of water was present in film B and in certain areas of film A. It was removed from both films completely through drying. Combined with the conductivity data, the greater amount of interlayer water in film B likely caused more extensive oxidation due to easier oxygen access or hydrolysis in film B than in film A, causing film B to lose conductivity to a greater degree than film A.

To confirm this, films A and B were dried in a vacuum at 200 °C for 24 h and then recharacterized. The drying conditions were identical to the previous treatment of film A. Figure 2a shows that both films recovered some of the conductivity lost over time after drying. In Fig. 2b, the peaks in the XRD plots of the two films post-drying are virtually identical and match peaks in film A pre-drying. This shows that conductivity recovery is likely caused by the removal of interlayer water via drying under vacuum for both films and the decrease of the *d*-spacing to 9.8 Å. Conductivity was not restored completely, likely because of oxidation over time and oxide formation between the layers. However, film A shows that drying both at the time of synthesis and after 5 years can result in 95% conductivity retention over that span. In addition, the XRD of film A pre-drying shows that there was still interlayer water after drying at the time of synthesis. However, if dried to the point where water is completely removed right after synthesis, even better stability than what film A demonstrated could be attained.

Films A and B were etched with hydrofluoric acid and sulfuric acid, and they exhibited superior conductivity to other films etched with hydrofluoric acid and hydrochloric acid. This method of using sulfuric acid produces clean surfaces. Hydrochloric acid, on the other hand, produces some chlorine terminations, which increase interlayer spacing and may hydrolyze when water is imbibed due to the reactivity of the Ti–Cl bond [24]. It has been known that HF/H_2SO_4-etched $Ti_3C_2T_x$ exhibits superior conductivity, but this work shows that the difference in conductivity is preserved for five-year-old films (Fig. S2). The advantage of HF/HCl is that the yield is high, currently ~ 75 wt% [10], and the current methods using HF/HCl can produce $Ti_3C_2T_x$ with a conductivity of 20,000 S cm^{-1} [10], which is desired for most applications. However, if $Ti_3C_2T_x$ with extreme conductivity and stability is desired, etching with HF/H_2SO_4 or at least washing with H_2SO_4 to protonate the surface after synthesis could be an option.

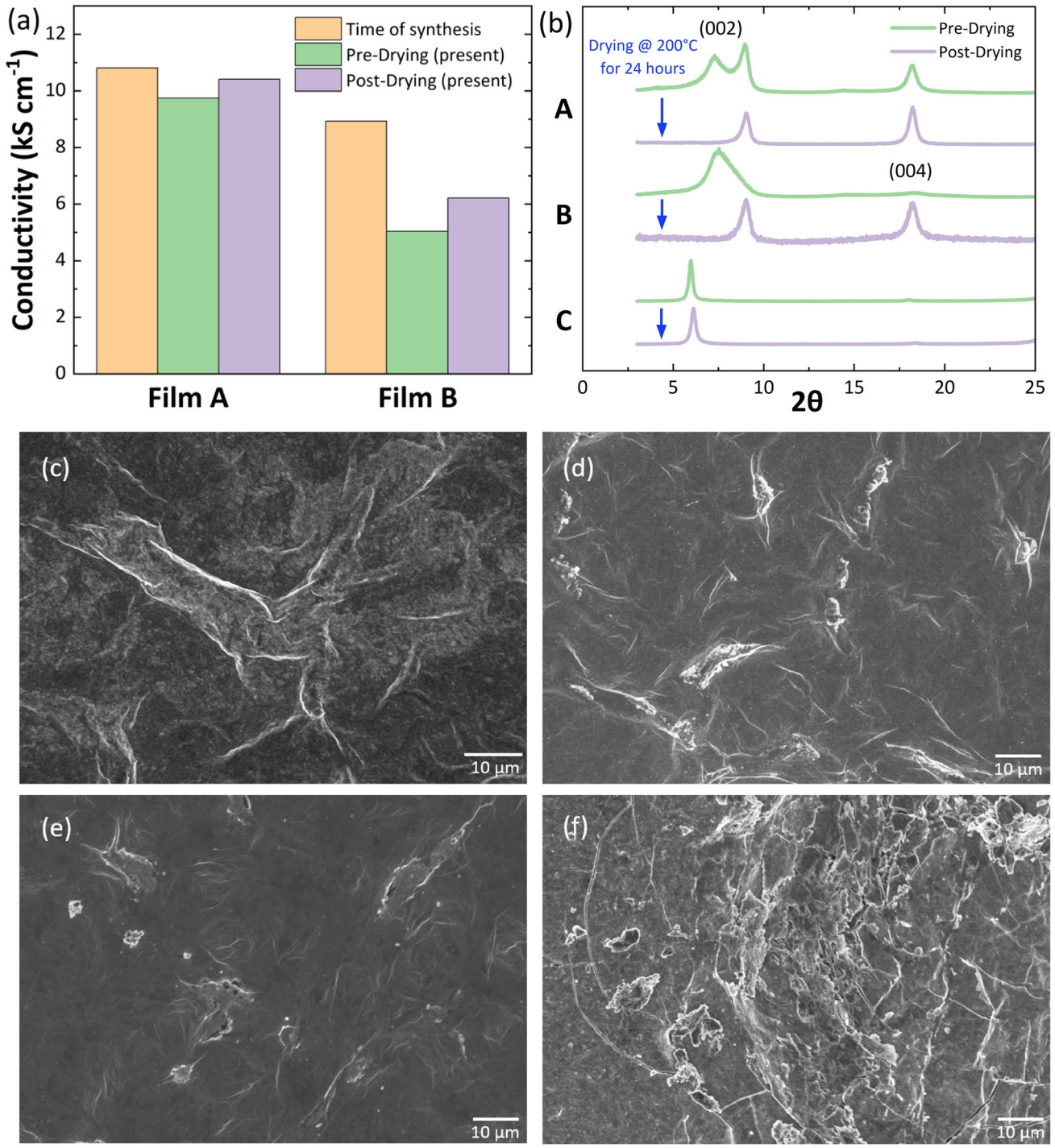

Fig. 2 **a** Comparison of conductivity of film A and film B at the time of synthesis, present-day before drying, and present-day after drying at 200 °C for 24 h under vacuum. **b** XRD patterns of films A, B, and C both before and after drying at 200 °C for 24 h under vacuum. SEM images of films A (**c**), B (**d**), and C (**e**, **f**)

Scanning electron microscopy analysis was conducted on films A, B, and C. The SEM images of all films show a smooth surface throughout most, if not all, of the area; however, in film C, some areas showed a rough, disjointed surface with cracks and peeled-off layers. The method of delamination of film C is the likely cause. It was delaminated with tetramethylammonium hydroxide (TMAOH), a large organic molecule exceptionally adept at exfoliating multi-layer MXene into single layers [32]. TMAOH is a versatile delaminating chemical, able to delaminate a wide variety

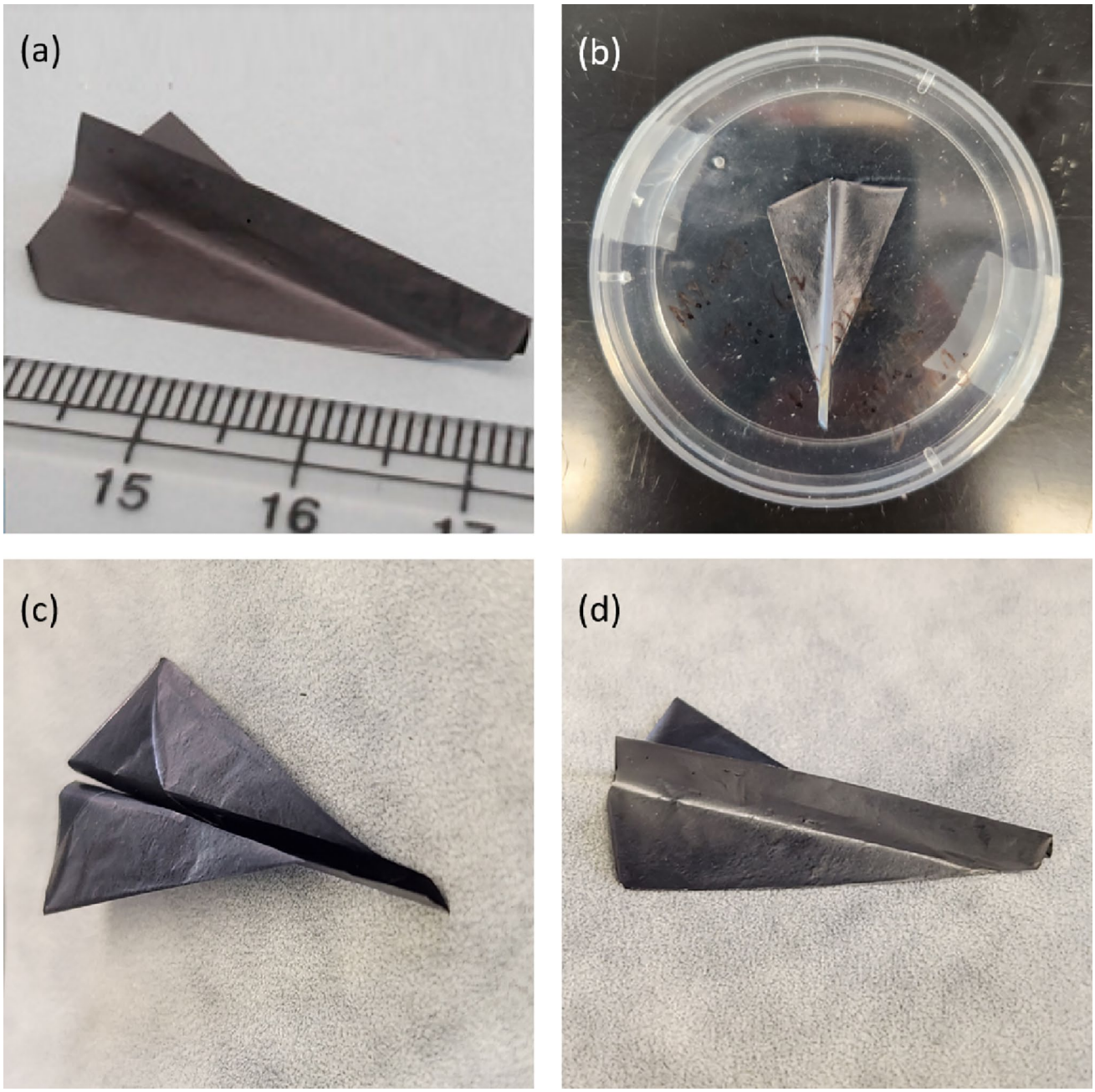

Fig. 3 Photographs of a $Ti_3C_2T_x$ paper plane from 2014 [33]. **a** At the date of synthesis[33]. **b** Stored in a petri dish since 2014. **c** Before drying. **d** After drying at 200 °C for 24 h to remove water

of MXenes. Still, one downside is that the TMA^+ ions that intercalate between the MXene layers to induce delamination are challenging to remove, thus resulting in a larger interlayer spacing than usual and easy water and air access to MXene surfaces. XRD of film C in Fig. 2b, with a single (002) peak at ~ 6°, showed a *d*-spacing of 14.7 Å, larger than either film A or B. In addition, the peak did not return to the position typical for the water-free film. It shifted by only about 0.1° after drying due to the continued presence of TMA^+ ions. The conductivity of film C increased from 32 to 77 S cm^{-1}, showing a significant increase after water loss. In the MXene V_2CT_x, the larger interlayer spacing was shown to lower the conductivity values, with a maximum of 140 S cm^{-1} [11]. In aged MXene films, the decrease in conductivity caused by a large interlayer spacing can be compounded by the increase in interlayer water permeation and oxidation

rate due to said large interlayer spacing. In addition, film C, delaminated with TMAOH, was likely made of MXene etched with a 50 wt% HF solution [32], which would result in smaller flakes and poorer conductivity than the 5 wt% HF solution used for films A and B [23, 24]. As shown by comparing these films, the choice of etchant and delamination method has a large effect on their stability and conductivity.

One of the oldest published MXene foil samples available at Drexel was a $Ti_3C_2T_x$ thin film fabricated in early 2014 and folded into a paper plane to demonstrate its flexibility and foldability [33]. At the time of synthesis, it exhibited a conductivity of 2,400 S cm^{-1} [33]. Remeasuring the conductivity about a decade later yields a value of 403 S cm^{-1}, a sixth of its original value, though Figs. 3b, c show that its original appearance was maintained well, and hardly any change could be visually observed. After drying at 200 °C for 24 h, the $Ti_3C_2T_x$ plane doubled its conductivity, reaching 849 S cm^{-1}, over a third of its original conductivity value. The role of removing water is shown here, as even conductivity loss over a decade could be significantly reversed. In addition, the sample displayed stability, as its shape or appearance did not change, and it retained metallic conductivity over a decade. Take into account that was the earliest stage of MXene research when the quality of the delaminated $Ti_3C_2T_x$ was nowhere near the one we have today. Since then, many developments have served to increase the stability of MXenes. We expect that stoichiometric $Ti_3C_2T_x$ that showed no degradation for 2 months as single-layer flakes on a substrate [34] or over 10 months in dilute solution [10] will have a lifetime in the ambient environment well over a decade when processed into a film and dried to remove the interlayer water.

Based on the demonstrated differences in stability exhibited by the MXene films in this study, one follow-up research direction could be a deeper investigation into the mechanism of degradation of the aged films through microscopic and spectroscopic characterization. This could confirm the suggested relationship between interlayer water and film oxidation, as well as, eventually, reveal other contributing factors to MXene film degradation. This article shows that $Ti_3C_2T_x$ can have a lifetime in the air sufficient for numerous applications. Future studies should focus on compositional and morphological changes in the MXene films with time.

4 Conclusions and outlook

This work focuses on the characterization of $Ti_3C_2T_x$ MXene films produced over the past 10 years to demonstrate their stability and identify the factors that contribute to it. Electrical conductivity measurements were made to quantify the effect of degradation over time. The etching and delamination conditions greatly affect the films' stability. When prepared with the best practices using a mild etchant, vacuum-dried $Ti_3C_2T_x$ can retain virtually all its conductivity after years of storage. Central to the stability of these films over time is control of the interlayer spacing, as a small interlayer spacing prevents water and air from entering and facilitating oxidation and degradation. On the other hand, alkylammonium cations (e.g., from TMAOH or TBAOH) increase the interlayer spacing and provide access to water and oxygen, leading to degradation of the films over time. Using milder etchants such as LiF/HCl with 5 wt.% equivalent of HF that decrease the concentration of defects and yield larger flakes, compared to using 50 wt% HF that was popular in the first few years of MXene research, also prolongs the lifetime of MXene films.

HF/H_2SO_4-etched $Ti_3C_2T_x$ displayed remarkable stability with 90% of initial conductivity (~ 10,000 S cm^{-1}) after 5 years in the laboratory environment. This suggests that clean surfaces with no chlorine terminations or residual aluminum salts lead to the highest environmental stability. Chlorine and fluorine surface terminations may hydrolyze over time if water can access the interlayer spacing and create nucleation sites for oxide formation. A decrease in interlayer spacing after drying at elevated temperatures resulted in MXene films that retained high conductivity. This method can be used to produce highly conductive and environmentally stable MXene. Drying at 200 °C and higher temperatures is a simple and powerful tool to increase the stability of MXenes. It removes interlayer water and welds the MXene layers together, guarding against future degradation.

The fact that drying can restore the conductivity of aged MXene films suggests that the observed decrease in conductivity is mainly due to water penetration between the hydrophilic MXene layers, not necessarily the degradation of MXene. When oxidation or hydrolysis products (titanium oxides) are formed between MXene sheets, the lattice spacing cannot be recovered by drying. We anticipate that polymer coatings or other packaging methods used in the semiconductor industry that protect the material from humidity can greatly prolong the lifetime of MXene films.

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Author contributions A.L. wrote the main manuscript text; collected data for Fig. 1 and Fig. 2; and prepared the figures (sans Fig. 3a). M.A.

collected and organized the samples used and provided guidance. M.S. collected data for Fig. 2b and provided guidance. Y.G., the PI of the laboratory, oversaw the research effort. All authors reviewed and edited the manuscript.

Data availability No datasets were generated or analyzed during the current study.

Declarations

Conflict of interest The authors declare no competing interests.

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