MXenes comprise a new class of solution-dispersable, 2D nanomaterials formed from transition metal carbides and nitrides such as Ti$_3$C$_2$. Here, it is shown that 2D Ti$_3$C$_2$ can be assembled from aqueous solutions into optical quality, nanometer thin films that, at 6500 S cm$^{-1}$, surpass the conductivity of other solution-processed 2D materials, while simultaneously transmitting >97% of visible light per-nanometer thickness. It is shown that this high conductivity is due to a metal-like free-electron density as well as a high degree of coplanar alignment of individual nanosheets achieved through spin coating. Consequently, the spin coated films exhibit conductivity over a macroscopic scale that is comparable to the intrinsic conductivity of the constituent 2D sheets. Additionally, optical characterization over the ultraviolet-to-near-infrared range reveals the onset of free-electron plasma oscillations above 1130 nm. Ti$_3$C$_2$ is therefore a potential building block for plasmonic applications at near-infrared wavelengths and constitutes the first example of a new class of solution-processed, carbide-based 2D optoelectronic materials.

1. Introduction

Research in 2D materials has proliferated since the discovery of practical methods to isolate graphene$^{[1-4]}$ and has since expanded to encompass boron nitride$^{[5]}$, transition metal dichalcogenides$^{[6]}$, layered double hydroxides$^{[7]}$, and transition metal carbides$^{[8]}$. The present study focuses on one representative of a class of transition metal carbides and nitrides known collectively as MXenes.$^{[9-14]}$ MXenes get their name from the MAX phases they are derived from and their similarity to graphene.$^{[9]}$ The MAX phases have the general formula $M_{n+1}AX_n$, where $n = 1, 2,$ or $3$, $M$ is an early transition metal, $A$ is a main-group element, and $X$ is carbon and/or nitrogen.$^{[15]}$ To produce MXenes, the $A$ element—Al in this case—which resides between stacks of $M_{n+1}X_n$ layers—is selectively etched, leaving behind oxygen, hydroxyl, and fluoride surface-terminating groups (Ti)$^{[19,16]}$. In appropriate solvents, the layers can be subsequently delaminated to form colloidal solutions of suspended $M_{n+1}X_n$, or “MXene,” nanosheets.$^{[17]}$ This work studies Ti$_3$C$_2$, one representative of more than a dozen 2D MXenes already discovered, with a vast family of possible compositions yet to be explored.$^{[9-11,18]}$ MXene, particularly Ti$_3$C$_2$, has demonstrated outstanding performance as an electrode material for supercapacitors with volumetric capacitance as high as 900 F cm$^{-3}$$^{[16]}$ and Li battery electrodes with capacities of 450 mA h g$^{-1}$.$^{[17]}$

In contrast to the existing applications of MXene, optical materials require nanometer-scale control over sample thickness and uniformity over wide areas. Preliminary optical studies of MXenes were previously possible only by employing physical vapor deposition.$^{[19]}$ In the present study, spin coating was used to fabricate continuous, optical-quality, conductive, thin films making it possible to measure the fundamental optical and electrical properties of solution-processed, substrate-aligned Ti$_3$C$_2$T$_x$ films. Separate percolative and bulk-like transport regimes are identified as a function of film thickness and the bulk in-plane conductivity is determined to be $6500 \pm 800$ S cm$^{-1}$, a value that is substantially larger than previous studies of Ti$_3$C$_2$T$_x$. Hall effect measurements are used to determine the fundamental electronic properties of mobility (0.9 cm$^2$ V$^{-1}$ s$^{-1}$) and charge-carrier density ($3.1 \times 10^{22}$ cm$^{-3}$) for films of this composition and structure. The complex optical dielectric function is measured, identifying free-plasma oscillations in the near-IR, suggesting the utility of these materials for plasmonics and making it possible to compare local, optical conductivity with long-range, DC conductivity. Finally, with an eye toward future optoelectronic applications, various figures of merit are calculated and the stability of the films to atmospheric gases is measured.

2. Results and Discussion

2.1. Structure of Spin coated Ti$_3$C$_2$T$_x$, Films

Previously we described two different synthetic approaches for preparing dispersions of 2D Ti$_3$C$_2$T$_x$ nanosheets, one

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employing hydrofluoric acid (HF) as the etchant, and another employing lithium fluoride (LiF) in concert with hydrochloric acid (HCl) to form HF in situ. The LiF/HCl method has the advantage of being less hazardous and both approaches lead to qualitatively similar aqueous dispersions. However, the surface-terminating groups, which are predicted to significantly impact the electrical properties of MXene, are expected to differ in the two cases: higher HF concentration yields a higher density of fluoride over hydroxides. For the present study, the LiF/HCl based synthesis was used, which was shown by transmission electron microscopy (TEM) to yield single, and few layer, Ti$_3$C$_2$T$_x$ sheets with lateral dimensions of hundreds of nm. Employing such dispersions as the starting material, films of varying thicknesses were spincast on to flat substrates (Figure 1; Figure S1, Supporting Information). To understand the degree to which 2D Ti$_3$C$_2$T$_x$ sheets reassemble into an ordered, lamellar solid in the spincasting process, the structure of the films was characterized by microscopy and X-ray diffraction (XRD). Scanning electron microscope (SEM) (Figure 2a,b; Figure S2, Supporting Information) and atomic force microscope (AFM) images (Figure 2c; Figure S3, Supporting Information) show continuous coverage of the substrates, even for films less than 10 nm in thickness, corresponding to just a few Ti$_3$C$_2$T$_x$ layers. These images exhibit a texture consistent with the single- or few-layer, Ti$_3$C$_2$T$_x$ constituents predominantly oriented parallel to the substrate. Higher contrast features observed every few micrometers are interpreted as protruding corners of flakes (Figure 2b,c; Figures S2 and S3, Supporting Information). The root-mean-square surface roughness, measured by AFM, ranges from 3 to 9 nm for films that range from 2 to 81 nm in thickness (Figure S3, inset, Supporting Information). This roughness is < $\lambda/20$ for all wavelengths of visible light, providing an operational definition of the “optical quality” of the films.

XRD patterns of both spin and dropcast MXene films were acquired and both display the typical family of 00$\ell$ peaks associated with the basal plane reflections (Figure 3). However the spincast films, which are less than 0.5 µm thick, exhibit a 002 peak that is 20 times more intense than that of the dropcast films, despite the fact that the latter are $\approx$ 2 orders of magnitude

Figure 1. Schematic of Ti$_3$C$_2$T$_x$ nanosheet (MXene) film fabrication. a) Ti$_3$C$_2$T$_x$ crystal structure. “T” represents surface terminations that are a mixture of F, O, and OH. b) Aqueous dispersions of Ti$_3$C$_2$T$_x$ can be deposited onto a variety of substrates via spincasting. c) Spincast Ti$_3$C$_2$T$_x$ film on glass.

Figure 2. Structural and morphological characterization of typical spincast Ti$_3$C$_2$T$_x$ films. a) SEM image of the profile of a cleaved film on Si-SiO$_2$. Scale bar is 300 nm. b) Surface SEM image of a film. Scale bar is 1 µm. c) AFM measurement to determine film thickness and surface roughness. Scale bar is 5 µm. A scratch is made in the Ti$_3$C$_2$T$_x$ film on Si-SiO$_2$. Left side shows Ti$_3$C$_2$T$_x$ surface and the right side (dark) shows exposed substrate. This film was 81 ± 2 nm thick with a surface roughness RMS of 8.7 nm.
thicker. This indicates a much higher degree of alignment of the basal planes of individual flakes parallel with the substrate plane, in agreement with the microscopy results and consistent with an orienting effect for high aspect-ratio nanomaterials in the shear forces present during spincasting.\(^\text{[23]}\)

2.2. Electrical and Optical Properties of Spincast Ti\(_3\)C\(_2\)Tx Films

To understand the transport properties of Ti\(_3\)C\(_2\)Tx, the sheet conductance of a set of films was measured and plotted against the thickness measured by AFM (Figure 4, red circles). A linear fit to these data provides a measure of the bulk conductivity of the spincast films of \(\sigma = 6600\ \text{S cm}^{-1}\), exceeding that of previously reported solution-processed films produced by vacuum filtration\(^\text{[24]}\) or rolling.\(^\text{[16]}\) Remarkably, this value is comparable to the conductivity obtained for Ti\(_3\)C\(_2\)Tx fabricated by etching physical-vapor-deposited Ti\(_3\)AlC\(_2\) films with HF.\(^\text{[19]}\) Also of importance is the fact that the conductivity remains linear with thickness for films thinner than 10 nm, demonstrating that the films retain a continuous network of overlapping nanosheets over cm\(^2\) areas even when only a few nanosheets in total thickness (a finding expanded upon in the discussion of percolation)\(^\text{[23]}\).

As the film becomes thinner, there must exist a threshold beneath which a dense network of overlapping flakes is not achieved and the conductivity becomes percolative. It has been shown previously that the onset of percolation can be determined by a power-law analysis of the sheet resistance versus transmittance of a set of samples using the following formula\(^\text{[25]}\)

\[
T = \left(1 + \frac{1}{\Pi(n)} \left(\frac{Z_0}{R_S}\right)^{\frac{1}{\Pi n}}\right)^{-2}
\]

where \(R_S\) is the sheet resistance, \(Z_0\) is the impedance of free space and has the value 377 \(\Omega\), and \(\Pi\) and \(n\) are the “percolative figure of merit” and the “percolation exponent,” respectively\(^\text{[25]}\).

The sheet conductance and transmittance were measured for 90 independently prepared samples and the transmittance translated into an estimated thickness. This data set was added to Figure 4 (solid black squares), where the logarithm of transmittance is represented by the upper axis and the derived thickness is represented by the lower axis. From a linear fit to these data, the bulk conductivity of the films was calculated to be \(\sigma = 6500 \pm 800\ \text{S cm}^{-1}\), in close agreement with the smaller, directly measured set. We note here that sheet conductance, measured in a dry \(N_2\) environment, drops by a factor of 3 when the films are exposed to atmospheric moisture (see below). Therefore, the DC conductivity values reported throughout were measured in a dry, \(N_2\)-filled glovebox, except where indicated otherwise.

To obtain a more statistically robust sampling of the trend in Figure 4, we sought a higher-throughput measurement of film thickness by AFM. The transmittance of a film is readily measured and can be seen in Figure 5 to vary with film thickness (measured by AFM). A plot of the logarithm of the transmittance at 550 nm versus measured thickness shown in Figure S4 (Supporting Information) exhibits a linear correlation over the range of film thicknesses of interest here as expected based approximately on the Beer–Lambert dependence of transmittance on thickness (the reduction in transmittance due to reflection is relatively smaller as shown in Figure S5 (Supporting Information) and roughly constant between different films). Taking advantage of this correlation, the thickness measured by AFM (\(\ell\)) can be translated into an estimated thickness. This data set was added to Figure 5 (solid black squares), where the logarithm of the transmittance is represented by the upper axis and the derived thickness is represented by the lower axis. From a linear fit to these data, the bulk conductivity of the films was calculated to be \(\sigma = 6500 \pm 800\ \text{S cm}^{-1}\), in close agreement with the smaller, directly measured set. We note here that sheet conductance, measured in a dry \(N_2\) environment, drops by a factor of 3 when the films are exposed to atmospheric moisture (see below). Therefore, the DC conductivity values reported throughout were measured in a dry, \(N_2\)-filled glovebox, except where indicated otherwise.

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When \( n \) is equal to zero this formula describes bulk transport, meaning that the conductivity is not thickness dependent, and \( \Pi \) becomes equal to \( 2 \sigma_{\text{DC}} / \sigma_{\text{OP}} \), where \( \sigma_{\text{DC}} \) and \( \sigma_{\text{OP}} \) are the DC and the optical conductivity values, respectively. \(^{[25]} \) Taking the data in Figure 4 and subjecting it to this analysis, we can determine where the percolative threshold begins. In Figure 6a, a linear trend is clearly seen on this log–log plot in the regime of \( 10^{-1000} \Omega^{-1} \), corresponding to a value of \( n \) equal to zero, i.e., bulk conductivity. In contrast above \( 1000 \Omega^{-1} \), the data clearly follow a different power law, indicating percolative transport. Separate values for the parameters of Equation (1) are determined by performing least-squares fits independently to both the bulk- and percolative-conductivity regimes, as shown in Figure 6b. For bulk conductivity to operate for a film of \( 1000 \Omega^{-1} \) and a value of the bulk conductivity of \( 6500 \ \text{S cm}^{-1} \) implies that films as thin as 2 nm are within the bulk-conductivity regime. This in turn indicates that spincoating yields densely electrically interconnected nanosheets even for average film thicknesses on the order of two monolayers. Arguing either from this observation—or from the fact that the sheet conductance remains linear with AFM-measured film thicknesses below 10 nm (Figure 4)—it is therefore appropriate to assign a bulk conductivity value to \( \text{Ti}_3\text{C}_2\text{T}_x \) in this geometry. In other words, the in-plane conductivity for spin-cast \( \text{Ti}_3\text{C}_2\text{T}_x \) does not change with film thickness for films greater than a few monolayers in thickness.

Having established that the spin-cast films are strongly oriented, and that this orientation leads to a higher bulk, in-plane conductivity that persists down to film thicknesses of a few layers, we now turn to measuring their fundamental optical properties. For independently prepared films of thickness ranging from 14 to 75 nm, the real and imaginary components of the dielectric constants, given by \( \varepsilon_1 \) and \( \varepsilon_2 \), respectively, were obtained by modeling the complex reflectivity data measured by spectroscopic ellipsometry (Figure 7). The optical models are qualitatively similar at all three thicknesses, though there are some quantitative differences for the thinnest film. Strikingly, \( \varepsilon_1 \) becomes negative at wavelengths greater than 1130 nm, indicating the onset of free carrier oscillations. Indeed the complex reflectivity can be accurately modeled as a Drude oscillator with a conductivity ranging from 9000 to 5000 S cm\(^{-1} \), or an average value of \( 7000 \pm 2000 \ \text{S cm}^{-1} \) (see details in Figure S6 in the Supporting Information). It follows that \( \text{Ti}_3\text{C}_2\text{T}_x \) is a plasmonic material at near-infrared wavelengths, a critical range for optical communication, biological imaging, chemical sensing, and thermal management.\(^{[26,27]} \) This conclusion is in accord with, and extends, previous work showing that surface plasmon polaritons (SPPs) could be excited in isolated, multilayer MXene stacks at terahertz/mid-infrared frequencies using electron energy loss spectroscopic microscopy.\(^{[28]} \)
Hall-effect measurements revealed both the origins of the high conductivity and plasmonic behavior of these films and point toward further improvements (Table 1; Figures S7 and S8, Supporting Information). The measured carrier concentration obtained assuming single band transport is $(3.1 \pm 0.7) \times 10^{22} \text{ cm}^{-3}$, on the same order of magnitude as bulk metals. However, the Hall-effect mobility at room temperature, $0.9 \pm 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, is lower than typical metals. It is not known presently whether inter- or intraflake transport limits the Hall-effect mobility. However, a comparison of the conductivity measured by four-point probe and that obtained from the Drude model is suggestive in this regard. To make the comparison, we first note that the ellipsometry measurement, which yields a conductivity of $7000 \pm 2000 \text{ S cm}^{-1}$, was performed in the open atmosphere. Therefore, the appropriate comparison is to the open-air-measured DC conductivity, which is $\approx 2000 \text{ S cm}^{-1}$. The optical measurement probes local, short-range, i.e., intraflake processes. This can be seen by noting that the carrier-scattering length (or mean free path) at optical frequencies—calculated from the optically modeled conductivity—is $3.1 \pm 0.7 \times 10^7 \text{ cm}$, on the order of magnitude as bulk metals. This means that the carrier scattering length is greater than the lateral dimensions of the flakes. Although not identical, the observation that the optical and DC conductivities agree to within a factor of 3 is noteworthy, suggesting intraflake processes predominantly limit the overall transport in both measurements. This conclusion is further corroborated by recent measurements of conductivity in single flakes of Ti$_3$C$_2$Tx, which show comparable mobilities and carrier densities to the present study (see Table 1).[29] However, the factor of 3 discrepancy in the optical and DC conductivity values still leaves open the possibility that interflake processes place further limits on long-range transport.

### 2.3. Technological Merits of Spincast Ti$_3$C$_2$Tx Films

As a means to understand the technological opportunities and challenges of these materials, we consider various figures of merit for plasmonic and transparent conducting applications and examine the stability of spincast Ti$_3$C$_2$Tx films to oxygen. To our knowledge, titanium carbides have not previously been considered for optical plasmonic applications. For these applications, $\varepsilon_2$, associated with dissipative losses, must be low.[26,30] Comparing Ti$_3$C$_2$Tx to other materials favored for near-infrared plasmonic applications, such as titanium nitride (TiN) and aluminum-doped zinc oxide (AZO),[27,30–33] the value of $\varepsilon_2$ at the important optical communication wavelength of 1550 nm is 14, which is half that of TiN[21] and much higher than AZO[30] (Figure S9, Supporting Information).

However, since $\varepsilon_1$ and $\varepsilon_2$ can be coupled to each other, it is more informative to construct figures of merit to compare materials for specific applications. Two key examples are localized surface plasmon resonance (LSPR) and SPP propagation, for which quality factors $Q_{\text{LSPR}}$ and $Q_{\text{SPP}}$ are used.[30] $Q_{\text{LSPR}}$ is defined as $[\varepsilon_1(\omega)\varepsilon_2(\omega)]$ where higher values correspond to narrower, longer-lived plasmon resonances for a hypothetical symmetric nanosphere of a given material. $Q_{\text{SPP}}$ is defined as $[\varepsilon_1(\omega)\varepsilon_2(\omega)]$. Both quality factors describe the enhancement of the local field at the surface of the plasmonic material relative to the incident field. Figure S7 (Supporting Information) compares the Ti$_3$C$_2$Tx figures of merit to those of TiN, AZO, and gold, demonstrating a slight advantage for the MXene in SPP applications relative to AZO, but substantially lower values than TiN and gold. These quality factors are shown only to gauge the magnitudes of the permittivity values; in order to go further and predict the plasmon resonance behavior of a 3D object made from a 2D MXene, its anisotropic properties would have to be accounted for. Nonetheless, it is remarkable that the $\varepsilon_2$ value measured herein, which depends on the electron scattering time and thus is extremely sensitive to film quality, compares favorably with any vapor-deposited films. As recognized for graphene,[34,35] the intrinsic 2D geometry of MXenes is requisite for a variety of plasmonic and metamaterial applications. However, unlike graphene plasmons, metallic Ti$_3$C$_2$Tx does not require doping or carrier injection from an electrode.

As mentioned above, exposure to the ambient atmosphere influences the electrical properties of the spincast films. In order to isolate the effect of humidity, their sheet conductances were measured in a sequence of hydrating and dehydrating conditions, while excluding O$_2$ (Figure 8a). The conductance was measured for a set of three films of different thicknesses immediately after spincasting them from aqueous solution in open air (blue), and then after being subjected to the following conditions: overnight storage under dry nitrogen (red), storage for 2 d under N$_2$ saturated with water vapor (purple), and a second overnight storage under dry N$_2$ (orange). Dehydrating the films dramatically increases their sheet conductance, and this hydration and dehydration effect is reversible. Previously dried films that are exposed either to moisture-saturated N$_2$ or open air, return to their as-fabricated, sheet conductance within 2 d. Since the as-fabricated state is measured immediately after spincasting from water, this can be considered the water-equilibrated value. Most of this change occurs quickly on exposure to air, with the conductance decreasing by a factor of three within less than 1 min (Figure 8b).

In order to observe the short-term effect of O$_2$, the same films were stored in the open atmosphere for 2 d and then under dry N$_2$ for a day, shown by green and yellow bars in Figure 8a, respectively. The effect seen in open atmosphere storage closely matched the trend seen in wet nitrogen, indicating the greater influence of water relative to O$_2$ on film properties over these time scales. This trend was common to films of different thicknesses (as indicated by their respective transmittance values in Figure 8a). Degradation of a film’s conductivity in open air did not have an effect on its transmittance (Figure S10, Supporting Information).

The spincast films deposited under ambient conditions, on select substrates, have potential for transparent conductor

### Table 1. Charge carrier properties measured by the Hall effect under vacuum compared to previously reported single flake measurements.

<table>
<thead>
<tr>
<th></th>
<th>Spincast Ti$_3$C$_2$Tx</th>
<th>Single-flake measurement from ref. [29]</th>
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</thead>
<tbody>
<tr>
<td>Carrier density [$\text{cm}^{-3}$]</td>
<td>$(3.1 \pm 0.7) \times 10^{22}$</td>
<td>$(8 \pm 0.3) \times 10^{21}$</td>
</tr>
<tr>
<td>Carrier mobility [$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]</td>
<td>$0.9 \pm 0.1$</td>
<td>$0.7 \pm 0.2$</td>
</tr>
<tr>
<td>Conductivity [$\text{S cm}^{-1}$]</td>
<td>$4000 \pm 400$</td>
<td>$900 \pm 300$</td>
</tr>
</tbody>
</table>
Figure 8. Air stability and flexibility of spincast films. a) Sheet conductance of three films in a sequence of wetting and drying. Films were measured as deposited (blue) then after storage in the following sequence of atmospheres: dry \(N_2\) overnight (red), wet \(N_2\) for 2 d (purple), dry \(N_2\) for 1 d (orange), open atmosphere for 2 d (green), and finally dry \(N_2\) for 1 d (yellow). b) Sheet conductance versus time for a film taken from dry \(N_2\) into open air. The red data point represents the sheet conductance measured in dry \(N_2\). The black curve represents the sheet conductance measured in open air. c) Picture of a film deposited on a flexible polyetherimide polymer substrate.

MXene nanosheets can be replicated over macroscopic areas. With new MXenes being discovered at a rapid pace this is likely the forefront of a new class of 2D optoelectronic materials with desirable properties for a wealth of applications.

4. Experimental Section

Detailed experimental information is available in the Supporting Information.

Supporting Information

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

Acknowledgements

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3. Conclusions

The highly conductive, optical-quality, flexible films demonstrated herein were produced using low-cost, water-based solution-processing steps and a scalable top-down nanomaterials synthesis approach. In Ti₃C₂Tx, the high carrier concentration enables both DC and plasmonic applications, in some examples exceeding what is possible for graphene or vapor-deposited materials. It is especially noteworthy that the conductivity measured optically—and therefore representing electron transport within single nanosheets—is of the same order of magnitude as the macroscopic, in-plane conductivity. This suggests that the remarkable electrical and optical properties of the constituent MXenes can be replicated over macroscopic areas. With new MXenes being discovered at a rapid pace this is likely the forefront of a new class of 2D optoelectronic materials with desirable properties for a wealth of applications.