Size-Dependent Physical and Electrochemical Properties of Two-Dimensional MXene Flakes

Kathleen Maleski,†‡§ Chang E. Ren,†§ Meng-Qiang Zhao,†‡ Babak Anasori,†© and Yury Gogotsi†©

1. INTRODUCTION

Two-dimensional (2D) materials, such as graphene, transition-metal carbides (MXenes), often exhibit large lateral-size polydispersity in delaminated colloidal solutions. This heterogeneity results in challenges when conducting fundamental studies, such as investigating correlations between properties and the 2D flake size. To resolve this challenge, we have developed solution-processable techniques to control and sort 2D titanium carbide (Ti3C2Tn) MXene flakes after synthesis based on sonication and density gradient centrifugation, respectively. By tuning the sonication conditions, Ti3C2Tn flakes with varied lateral sizes, ranging from 0.1 to ~5 μm, can be obtained. Furthermore, density gradient centrifugation was used to sort Ti3C2Tn flakes with different lateral sizes into more monodisperse fractions. These processing techniques allow for the characterization of size-dependent optical and electronic properties by measuring the absorption spectra and film conductivity, respectively. Additionally, by testing the material as electrochemical capacitor electrodes, we show the Ti3C2Tn flake-size dependence of electrochemical performance. Ti3C2Tn films made of flakes with lateral sizes of ~1 μm showed the best capacitance of 290 F/g at 2 mV/s and rate performance with 200 F/g at 1000 mV/s. The work provides a general methodology which can be followed to control the size of MXenes and other 2D materials for a variety of applications and fundamental size-dependent studies.

KEYWORDS: two-dimensional material, MXene, flake size, sonication, density gradient centrifugation

ABSTRACT: Two-dimensional (2D) particles, including transition metal carbides (MXenes), often exhibit large lateral-size polydispersity in delaminated colloidal solutions. This heterogeneity results in challenges when conducting fundamental studies, such as investigating correlations between properties and the 2D flake size. To resolve this challenge, we have developed solution-processable techniques to control and sort 2D titanium carbide (Ti3C2Tn) MXene flakes after synthesis based on sonication and density gradient centrifugation, respectively. By tuning the sonication conditions, Ti3C2Tn flakes with varied lateral sizes, ranging from 0.1 to ~5 μm, can be obtained. Furthermore, density gradient centrifugation was used to sort Ti3C2Tn flakes with different lateral sizes into more monodisperse fractions. These processing techniques allow for the characterization of size-dependent optical and electronic properties by measuring the absorption spectra and film conductivity, respectively. Additionally, by testing the material as electrochemical capacitor electrodes, we show the Ti3C2Tn flake-size dependence of electrochemical performance. Ti3C2Tn films made of flakes with lateral sizes of ~1 μm showed the best capacitance of 290 F/g at 2 mV/s and rate performance with 200 F/g at 1000 mV/s. The work provides a general methodology which can be followed to control the size of MXenes and other 2D materials for a variety of applications and fundamental size-dependent studies.

Received: March 21, 2018
Accepted: June 29, 2018
Published: June 29, 2018

© 2018 American Chemical Society

DOI: 10.1021/acsami.8b04662
ACS Appl. Mater. Interfaces 2018, 10, 24491–24498
ACS Applied Materials & Interfaces
sedimentation rates.\textsuperscript{18,19} In particular, density gradients have also been utilized to separate 2D materials such as transition metal dichalcogenides (TMDs, such as MoS\textsubscript{2}),\textsuperscript{20} and graphene by number of layers,\textsuperscript{19} sheet size, and surface chemistry.\textsuperscript{19,22} In this regard, sonication and density gradient methods are promising to control or sort the lateral size of MXenes to allow studies on their size-dependent properties.

In this study, these two methods are explored to control the flake size of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene. First, we discuss the sonication conditions to achieve control over the lateral size of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene flakes. Additionally, we use inexpensive and environmentally friendly sucrose as the main component in a density gradient separation\textsuperscript{22−24} to isolate Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} flakes with different sizes by centrifugation. Using this principle to create controlled dispersions, we probed the relationships between lateral size of the nanosheet and the resulting optical, electrical, and electrochemical properties.

2. EXPERIMENTAL METHODS

2.1. Preparation of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene. Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} powder was obtained from etching of Ti\textsubscript{3}AlC\textsubscript{2} MAX powder (<38 \textmu m particle size), whose synthesis method is described in the literature.\textsuperscript{1} In detail, 1 g of LiF powder was added to 20 mL of 9 M hydrochloric acid solution and stirred for 5 min for dissolving. Then, 1 g of Ti\textsubscript{3}AlC\textsubscript{2} powder was slowly added to the mixture at room temperature; the process was operated over 10 min to prevent overheating. Then, the mixture was kept stirring at 500 rpm at 35 °C for 24 h. After the reaction, about 50 mL of deionized water was added to the mixture and centrifuged at 3500 rpm for 5 min to separate the supernatant from Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} sediment. The washing step was repeated 5–6 times until the color of the supernatant became dark green (pH around 6). Then, the centrifuge time was extended by 1 h to separate the sediment, which was dispersed with deionized water. Then, the mixture was subjected to hand shaking for 10 min and centrifuged at 3500 rpm for 1 h. The collected supernatant contained large Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} flakes (marked as BS-0). The sediment was vacuum filtered on a Celgard film (0.25 \textmu m pore size, 3501 Catted PP, Celgard) and dried at room temperature under vacuum for further usage as multilayered Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} powder.

To get sonicated Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} flakes, 0.2 g of multilayered Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} powder obtained as described above was mixed with 50 mL of water and bath-sonicated (Branson 2510 Ultrasonic Cleaner, 100 W) under flowing Ar gas in an ice bath for 0.5 s, 1.5, or 3 h, respectively. For probe-sonicated samples, the Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} powder in water was probe-sonicated (Fisher Scientific model 505 Sonic Dismembrator, 500 W) for 1 h under pulse setting (8 s on pulse and 2 s off pulse) at an amplitude of 50% in an ice bath. All of the sonicated solutions were centrifuged at 3500 rpm for 60 min, and the supernatant was collected, respectively.

To make a Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} film, a Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} colloidal solution, which contained 5 mg of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} flakes, was deposited by vacuum-assisted filtration on a Celgard film. After the filtered film was dried in ambient environment, a free-standing Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} film was detached from the substrate and directly used as electrode in supercapacitors.

2.2. Sucrose Density Gradient Centrifugation. Sucrose solutions were chosen as the separation media because of the environment friendliness, low cost, and viscous nature which are suitable for separating hydrophilic solutions of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} MXene. Typically, 20–60% (w/v) sucrose solutions were made with water (densities varied from 1.08 to 1.32 g/cm\textsuperscript{3}). The density gradient was formed by layering different density sucrose solutions on top of each other from highest density (bottom of centrifuge tube) to lowest density (top of centrifuge tube), depending on the volume of the total sucrose density gradient. The as-produced Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} supernatant was layered on top of the sucrose density gradient and centrifuged at 3500 rpm for 30 min. It is best to note that the conditions of the density gradient centrifugation depend largely on the starting solution and the desired separation (monodispersity). After centrifugation, a micropipette was used to manually sample 0.5–1.0 mL fractions along the centrifuge tube, depending on the desired quantity and polydispersity. The density gradient technique can be scaled up to separate enough materials to create free-standing films by layering a Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} solution (3 mL, >10 mg/mL) on top of a 9 mL density gradient (66 w/v %, 1 mL step volume and 60−20 w/v % 2 mL step volume). After separation (3500 rpm for 30 min), 3 mL fractions were vacuum filtered to create films composed of flakes with different lateral sizes. The samples are named based upon the line of the centrifuge tube (in milliliters) from which they were fractioned (e.g., 12−9 or 6−3 mL).

2.3. Characterization. X-ray diffraction (XRD) measurements were performed using a powder diffractometer (Rigaku SmartLab) with Cu K\textalpha radiation at a step of 0.02° and a collection time of 0.5 s per step. Transmission electron microscopy (TEM, JEOL JEM-2100F) was used to gather information about the size of the flakes as well as the flake-size distribution. Dynamic light scattering (DLS) was performed by pipetting 1 mL of solution into a polystyrene cuvette (Zetasizer Nano ZS, Malvern Instruments, USA). DLS average was taken over a total of five measurements from each sample. Characterization of optical properties was measured by UV−vis absorbance spectroscopy (10 mm optical path length cuvette, Evolution 201, Thermo Scientific), scanning from 200 to 1000 nm and normalized at 264 nm. Electrical properties were probed by measuring conductivity by a four-point probe technique (Jandel Engineering Limited). The distance between probes was 1.0 mm. Cross-section scanning electron microscopy (SEM) was conducted on a Zeiss Supra 50VP to measure the thickness of the free-standing electrodes.

2.4. Correlation of DLS and SEM Size Distributions. SEM samples were prepared by vacuum filtering low-concentration (<0.1 mg/mL) Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} colloidal solutions over a porous alumina membrane (Anodic, 0.1 \textmu m pore size, Whatman). SEM analysis was conducted at various magnifications. Microscopy-derived distributions were determined by measuring the length (longest distance) and width (shortest distance) of 100 flakes using ImageJ image analysis software,\textsuperscript{25} followed by using a histogram (30 bins from 0 to 6 \textmu m) to create log-normal distributions. Distributions were also calculated for SEM length and SEM width (Table 1). The largest DLS intensity peak by percentage (%) was named \textit{a}_{DLS}, similar to the

<table>
<thead>
<tr>
<th>sample</th>
<th>fit type</th>
<th>SEM length (nm)</th>
<th>SEM width (nm)</th>
<th>aspect ratio (SEM L to W)</th>
<th>SEM average (nm)</th>
<th>\textit{a}_{DLS} (nm)</th>
<th>Z-average (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>log-normal</td>
<td>912</td>
<td>527</td>
<td>1.371</td>
<td>693</td>
<td>568</td>
<td>622</td>
</tr>
<tr>
<td>2</td>
<td>log-normal</td>
<td>1670</td>
<td>941</td>
<td>1.775</td>
<td>1259</td>
<td>770</td>
<td>927</td>
</tr>
<tr>
<td>3</td>
<td>log-normal</td>
<td>1989</td>
<td>1381</td>
<td>1.440</td>
<td>1658</td>
<td>1039</td>
<td>1409</td>
</tr>
<tr>
<td>4</td>
<td>log-normal</td>
<td>2313</td>
<td>1462</td>
<td>1.582</td>
<td>1839</td>
<td>1148</td>
<td>1595</td>
</tr>
<tr>
<td>5</td>
<td>log-normal</td>
<td>3199</td>
<td>2022</td>
<td>1.582</td>
<td>2547</td>
<td>1231</td>
<td>2010</td>
</tr>
</tbody>
</table>

Table 1. Data for Correlations between Dynamic Light Scattering (DLS) and Scanning Electron Microscopy (SEM) for Various Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} Solutions
previous reports. Z-average and $d_{\text{DLS}}$ were used to compare to SEM distributions. Results for DLS are shown in Table 1.

2.5. Electrochemical Characterization. Various flake sizes were measured electrochemically by recording their performance in an asymmetric supercapacitor. Ti$_3$C$_2$T$_x$ electrodes were fabricated by vacuum filtering to create a film. The films were cut to size and used in a three-electrode Swagelok. The cell was structured as Ti$_3$C$_2$T$_x$ (working), over capacitive-activated carbon (counter), silver/silver chloride (Ag/AgCl) in 1 M KCl as the reference electrode, and glassy carbon discs as the current collectors, to avoid hydrogen evolution reactions. Electrochemical testing was performed in 3 M sulfuric acid (H$_2$SO$_4$) electrolyte because of the higher ionic conductivity compared to 1 M H$_2$SO$_4$. The performance of Ti$_3$C$_2$T$_x$ was evaluated using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge and discharge using a BioLogic VMP3 potentiostat (BioLogic, France). After initially precyling the electrodes at 20 mV/s for 500 cycles, CV was performed at scan rates from 2 to 10 000 mV/s. The BS-0.25 material was used to measure long-term cyclability at 10 A/g. The cell was cycled for 10 000 cycles with a 0.9 V potential window (−0.6 to 0.3 V vs reference).

3. RESULTS AND DISCUSSION

Detailed illustration of how the sonication and sucrose density gradient centrifugation techniques are utilized to control the size of MXene flakes after synthesis is shown in Figure 1.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (a) Schematic representation of a colloidal dispersion of MXene which is polydisperse in flake size. (b) Dynamic light scattering (DLS) intensity distribution showing the wide distribution of particle sizes (red arrows) in an as-synthesized MXene solution with no centrifugation. The size is represented as hydrodynamic diameter ($\tilde{d}$, nm) in nanometers. (c) Schematic showing sonication can be used as a method to decrease the particle size by varying the time (0.25−3 h) or the power (100−250 W). (d) Schematic of polydisperse MXene flakes which can be separated by 20−66 w/v % sucrose-density gradients.

Exfoliation or delamination of 2D materials produces heterogeneous dispersions with large degrees of polydispersity (nanometer to micrometer) and varying thicknesses (i.e., single- to multilayer flakes) (Figure 1a,b). When conducting Ti$_3$C$_2$T$_x$ synthesis, centrifugation is a key part of the procedure to isolate delaminated Ti$_3$C$_2$T$_x$ flakes from multilayered Ti$_3$C$_2$T$_x$ and the unreacted MAX phase particles that were used as the starting precursor. The as-synthesized Ti$_3$C$_2$T$_x$ solution is usually subjected to centrifugation at 3500 rpm for 1 h, removing the multilayer Ti$_3$C$_2$T$_x$ flakes and leaving a Ti$_3$C$_2$T$_x$ colloidal solution largely composed of single-layer flakes. On one hand, the size of Ti$_3$C$_2$T$_x$ flakes can be reduced by sonication, with control achieved by tuning the sonication time and power (Figure 1c). Another approach is the sucrose density gradient centrifugation, which renders the isolation of Ti$_3$C$_2$T$_x$ flakes with different lateral sizes (Figure 1d).

In the most simplistic manner, sonication is used to directly break the flakes in solution because of the input mechanical energy, producing Ti$_3$C$_2$T$_x$ lateral sizes which are smaller compared to the as-synthesized MXene (Figure 2). Depending on the sonication time and power, the Ti$_3$C$_2$T$_x$ solutions obtained by bath sonication at 100 W for 0.25, 1.5, and 3 h are denoted as BS-0.25, BS-1.5, and BS-3.0, respectively. The Ti$_3$C$_2$T$_x$ solution without sonication is denoted as BS-0, and the sample obtained by probe-sonication at 250 W for 1 h is denoted as PS-1.0. Figure 2 shows the resulting TEM images and distribution of flake size by percentage obtained by statistical analysis of over 300 flakes. The lateral size of Ti$_3$C$_2$T$_x$ flakes in the BS-0 ranges from 1.0 to 10.0 μm, with an average size of $4.4 \pm 1.5 \mu m$ (Figure 2a). Just after 0.25 h of sonication (BS-0.25), polydisperse flakes are reduced to smaller, more monodisperse flakes ranging from less than 0.5 to 2.5 μm, with an average size of $1.0 \pm 0.56 \mu m$ (Figure 2b). As expected, when bath sonication time is increased, Ti$_3$C$_2$T$_x$ continues to decrease in lateral size below 1 μm. The average flake sizes for BS-1.5 and BS-3.0 are $0.57 \pm 0.30$ and $0.35 \pm 0.15 \mu m$, respectively (Figure 2c,d). By introducing more power, probe sonication method produces the smallest and most monodisperse flakes (<0.5 μm), revealing an average size of $0.13 \pm 0.06 \mu m$ (Figure 2e).

Throughout processing by bath and probe sonication, the presence of (002) peak in the XRD patterns was used to ensure that the structure of Ti$_3$C$_2$T$_x$ was retained (Figure 2f). The XRD measurements were performed on Ti$_3$C$_2$T$_x$ films made by vacuum-assisted filtration from their colloidal solutions. The (002) peaks of Ti$_3$C$_2$T$_x$ films were at similar positions around 6.8°, indicating comparable interlayer spacing despite different flake sizes. Four-point probe measurements of vacuum-assisted filtered films of each condition indicated that the longer sonication times (smaller flakes) decreased the electrical conductivity (Figure 2g). It is hypothesized that the smaller flakes result in more interfacial resistance between flakes, leading to the overall reduced electrical conductivity. The concentration of defects may also increase with the sonication time, which may contribute to the reduced electrical conductivity. Films made by filtering the largest flakes (BS-0) exhibited the highest conductivity of ~5000 S/cm, whereas the films composed of the smallest flakes (PS-1.0) showed the lowest conductivity ~1000 S/cm. Smallers flakes stack more compactly and occupy smaller slits, and lead to increased density, which was also confirmed by density measurements (Figure 2h).

Furthermore, the density-gradient centrifugation can be used as another promising method to control the lateral size of MXene flakes. This method takes advantage of mass differences in Ti$_3$C$_2$T$_x$ flakes with different lateral sizes, which appear in the as-synthesized supernatant after centrifugation for 1 h at 3500 rpm (step 1 in Figure 3a). By placing the polydisperse solution on top of a density gradient solution and subjecting it to centrifugation (step 2 in Figure 3b), the density of the supernatant will be affected by the addition of sucrose, leading to a new density gradient that will separate the flakes into distinct layers based on their density. This method allows for the separation of flakes into different size classes, which can be further processed for various applications.
3a), flakes move at diverse rates based on the lateral size. Larger or thicker nanosheets have faster sedimentation rates than the smaller or thinner flakes, making fractionation after density gradient centrifugation an easy way to isolate flakes of each size.\(^{19}\) The fractions, which are isolated by pipetting known volumes of solution from the top of the centrifuge tube (e.g., 0.5, 1, or 3 mL fractions were used in this study), are noted as \(f_1\) to \(f_n\), where \(n\) stands for the number of fractions in the centrifuge tube. The smaller fraction numbers are located toward the top of the centrifuge tube (smaller flakes) and inversely, the larger fraction numbers are toward the bottom (larger flakes), correlating with the change in sucrose density along the tube (step 3 in Figure 3a). A digital image of a centrifuge tube (15 mL) after density gradient centrifugation is shown in Figure 3b, where bands are present because of different concentrations of Ti\(_3\)C\(_2\)T\(_x\) flakes moving along the density gradient at various rates.

The degree of monodispersity obtained from this method lies in optimizing the sucrose gradient as well as time and speed of centrifugation. We used the as-produced Ti\(_3\)C\(_2\)T\(_x\) flakes with no sonication (BS-0) and conducted the density gradient centrifugation at a centrifuge speed of 3500 rpm for 30 min. DLS of the BS-0 flakes revealed intensity distribution averages from 459 to 7460 nm, with the intensity size distribution increasing in peak position as the fraction numbers increased (Figure 3c).

Other 2D materials such as black phosphorus\(^{29}\) and TMDs (MoS\(_2\))\(^{30}\) show changes in optical absorbance spectra with respect to size because of differences in electronic structures associated with edge sites compared to the basal plane. To probe if the changes were exhibited in Ti\(_3\)C\(_2\)T\(_x\) solutions, the UV–visible absorption measurements of the density-gradient-separated solutions were conducted. After normalizing the spectra at 264 nm (Figure 3d), a trend was observed similar to the results reported on Ti\(_3\)C\(_2\)T\(_x\) sorted by cascading centrifugation.\(^{31}\) The smallest flakes obtained in the first fractions show an absorption peak at \(\sim 237\) nm and a broad absorption peak at 785 nm. Ti\(_3\)C\(_2\)T\(_x\) samples with larger flakes show similar absorption behavior to smaller lateral sizes; however, they show an additional peak around 375 nm, which may originate from TiO\(_2\), as smaller particles are less chemically stable and TiO\(_2\) nanoparticles were shown to decorate their edges.\(^{31}\) Furthermore, the height of the two UV peaks changes with respect to size, as the larger flakes exhibit a slightly higher absorbance at 375 nm. In general, the normalized absorption in the visible wavelength range decreases with decreasing flake size.

It is important to note that DLS theoretically assumes spherical particles, however, the DLS data can be correlated using microscopy-derived size distributions and has previously

**Figure 2.** Effect of sonication on flake size, structure, and properties. Flake-size distribution (graph) and transmission electron microscopy (TEM) image (inset) of (a) no sonication, (b) 0.25 h bath sonication, (c) 1.5 h bath sonication, (d) 3.0 h bath sonication, and (e) 1.0 h probe sonication. (f) X-ray diffraction (XRD) patterns of Ti\(_3\)C\(_2\)T\(_x\) without sonication and various bath sonication times. (g) Conductivity measurements of films with different densities and sonication times. The numbers in the figure represent the duration of sonication in hours.

**Figure 3.** Sucrose density gradient centrifugation of Ti\(_3\)C\(_2\)T\(_x\) MXene (a) schematic explaining the density gradient: Step 1: separate the supernatant from unreacted MAX phase and multilayered MXene sediment; step 2: create sucrose density gradient and layer MXene aqueous dispersion on top; step 3: centrifuge gradient at 3500 rpm for 30 min. (b) digital image of 20–66% sucrose density gradient (15 mL vial) separating Ti\(_3\)C\(_2\)T\(_x\) MXene; (c) Dynamic light scattering (DLS) intensity distributions of sucrose density gradient fractions; (d) UV–visible absorption spectra, normalized to 264 nm, of Ti\(_3\)C\(_2\)T\(_x\) colloidal solutions obtained by density gradient centrifugation.
been correlated for other 2D materials.26 By selecting Ti3C2T x samples of different sizes via density gradient centrifugation (Figure 4a,b) and deriving average log-normal particle size distributions (Figure 4c) by SEM, a general relationship can be observed (Table 1). By comparing the largest length measured in SEM images (labeled as SEM length) to the smallest length in SEM images (labeled as SEM width), the aspect ratio of Ti3C2T x flakes was determined to be in the range of 1.58–1.73, with the average aspect ratio of Ti3C2T x flakes ~1.6:1 (length/width). Moreover, comparing the SEM distributions to the DLS data, it can be observed that the Z-average value is most similar to SEM width distributions, suggesting we can use the in situ Z-average and the average aspect ratio to calculate the SEM width and SEM length, without performing expensive and time-consuming electron microscopy. This relationship can be used to support the DLS data with respect to size-dependent properties.

To study the effect of flake size on the electrochemical behavior of Ti3C2T x MXene, we vacuum-filtered the solutions after different sonication conditions (Figure 2) and the sucrose density gradient fractions to make Ti3C2T x films and used them as electrodes in an electrochemical capacitor (Figures 5 and 6). The electrodes had thicknesses of 1.3 μm (BS-0), 1.17 μm (BS-0.25), 1.19 μm (BS-1.5), 1.25 μm (BS-3.0), 1.47 μm (BS-10), ~0.400 μm (6–3), and ~0.825 μm (12–9), respectively. Cyclic voltammograms of the sonicated Ti3C2T x films at 20 mV/s in Figure 5a show a combination of pseudocapacitive and rectangular shape, similar to previous studies on Ti3C2T x.2,8,9,13 The redox peaks are associated with proton-induced pseudocapacitance, and the small cathodic and anodic peak potential separation (less than 60 mV) indicate that the redox process is highly reversible.2,9

The effect of sonication is two-sided: sonication breaks flakes into smaller sizes and may lead to the introduction of defects, which enables easier electrolyte diffusion and exposure to a larger number of active sites, respectively. However, smaller flakes have lower electrical conductivity because of more interfacial contact resistance and the higher number of defects introduced by sonication.15,32 Lower electrical conductivity diminishes the charge transfer and, thus, the capacitive performance and rate performance. Therefore, to optimize the electrochemical performance, a balance between the increase in active sites and the loss of electrical conductivity is required. For instance, the BS-0.25 sample showed the best capacitance of 293 F/g at a scan rate of 2 mV/s. The BS-0, BS-1.5, BS-3.0, and BS-10 electrodes offered similar capacitances of 270, 288, 270, and 260 F/g at 2 mV/s, respectively (Figure 5b), suggesting that the size may not play a critical role in the overall capacitance at low current rates. However, when comparing the rate performance, BS-3.0 Ti3C2T x film outperformed others, especially at scan rates above 1000 mV/s, with a capacitance retention of 70% from 2 mV/s to 1000 mV/s (Figure 5c). The electrode capacitance and a capacitance retention at 1000 mV/s were plotted versus the scan rate (Figure 5c). These results show that Ti3C2T x with median flake size ~1.6:1 (length/width) electrodes perform the best in terms of capacitance (~1.0 μm for BS-0.25) or rate performance (~0.35 μm for BS-3.0).

The redox peaks are associated with proton-induced pseudocapacitance, and the small cathodic and anodic peak potential separation (less than 60 mV) indicate that the redox process is highly reversible.2,9
show the best performance, with highest capacitance at 2 mV/s as well.

The slope of Nyquist plots at low frequency (Figure 5d) shows the difference in electrolyte diffusion resistance. The lowest diffusion resistance of BS-0.25 electrode can be attributed to a combination of relatively smaller flake size and high electrical conductivity. The 45° slopes of the BS-3.0 and PS-1.0 electrodes are shorter than others, which are due to the shorter ion-transport paths contouring the smaller flakes. All Nyquist plots have relatively small contact resistance around 1 Ω cm², which were due to the good electrical conductivity of the Ti₃C₂Tₓ electrodes. When the densities of electrodes are considered, Ti₃C₂Tₓ electrodes offered a volumetric capacitance as high as 1100 F/cm³ for BS-0.25 at 2 mV/s (Figure 5e), which is comparable with the previously reported Ti₃C₂Tₓ-based films. It is worth noting that the electrodes composed of sonicated flakes achieved volumetric capacitance compared with the non-sonicated electrodes because of their higher densities. Using the best-performing Ti₃C₂Tₓ film, BS-0.25, the device’s long-term cycling reveals stable performance over 10 000 cycles (Figure 5f).

In addition to testing the electrodes produced with Ti₃C₂Tₓ exposed to sonication, Ti₃C₂Tₓ obtained through sucrose density-gradient centrifugation was also fabricated into free-standing electrodes. DLS measurements revealed that the 12–9 mL fraction (top of centrifuge tube) was composed of nanoscale-sized flakes with a DLS peak of ∼400 nm, whereas the 6–3 mL fraction (near bottom of centrifuge tube) was primarily composed of larger flakes and exhibited a DLS peak of ∼1.7 µm (Figure 6a). Cross-section SEM (Figure 6b) showed the films had thicknesses of ∼400 and ∼825 nm, for the large-flake (6–3 mL) and small-flake (12–9 mL) electrodes, respectively, signifying that each fraction contained a different concentration of Ti₃C₂Tₓ in solution.

Ti₃C₂Tₓ separated in a density gradient showed similar CV profiles in comparison with the sonicated material (compare Figures 5a and 6c), and EIS displayed differences in resistance between the two electrodes made through density gradient separation (Figure 6d). The lowest resistance is revealed in the electrode composed primarily of larger MXene flakes (6–3 electrode), which can be explained by the increased electronic conductivity of the film. However, the film is also thinner, increasing the accessibility of the electrolyte and lowering the electrolyte diffusion resistance (Figure 6d). When comparing the gravimetric capacitance (F/g), the 6–3 electrode outperformed the other materials tested by achieving 319 F/g at 10 mV/s and 249 F/g at 1000 mV/s. Ti₃C₂Tₓ separated by density gradient with thinner electrodes also showed improved capacitance retention, especially at high scan rates (Figure 6f).

4. CONCLUSIONS

Sonication and sucrose density gradient centrifugation have been used to achieve control of the lateral size of polydisperse, aqueous colloidal solutions of 2D Ti₃C₂Tₓ MXene flakes. The Ti₃C₂Tₓ average flake sizes ranged from 0.13 to 4.4 µm by tuning the sonication time and power. Alternatively, sucrose density gradients provided a reliable method of sorting Ti₃C₂Tₓ flakes based on the lateral size. By probing the electrical, optical, and electrochemical properties of the sonicated and/or separated flakes, differences can be realized with respect to the lateral size of the Ti₃C₂Tₓ flakes. Decreasing the lateral flake size shifted the optical absorbance to lower absorbance values and smaller flake size resulted in decreased electrical conductivity of the filtered Ti₃C₂Tₓ films. However, smaller flake size enables better electrolyte accessibility to more active sites, which may be responsible for a slight increase in the electrochemical performance of Ti₃C₂Tₓ film electrodes. MXene films composed of ∼1.0 µm flakes showed a larger capacitance than that composed of ∼4.4 µm flakes, 288 versus 270 F/g. The film composed of ∼0.35 µm flakes showed the best capacitance retention of ∼70% when the scan rates increased from 2 to 1000 mV/s. Electrodes
composed of Ti$_3$C$_2$Tx obtained through sucrase density gradient centrifugation displayed 319 F/g at 10 mV/s and 249 F/g at 1000 mV/s. This study provides a method for obtaining MXene flakes with well-controlled sizes and can potentially provide a simple route for controlling the size for applications, where monodisperse fractions are necessary or when studying fundamental size-dependent properties of MXenes.

**AUTHOR INFORMATION**

**Corresponding Author**
*E-mail: gogotsi@drexel.edu.*

**ORCID**

Kathleen Maleski: 0000-0003-4032-7385
Babak Anasori: 0000-0002-1955-253X
Yury Gogotsi: 0000-0001-9423-0432

**Author Contributions**

K.M. and C.E.R. contributed equally to this work. The manuscript was written through contribution of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Research was sponsored by the Army Research Office and was accomplished under Cooperative Agreement Number W911NF-18-2-0026. Funding was provided by the U.S. Army via the Surface Science Initiative Program (PE W911NF-18-2-0026). Funding was provided by the U.S. Army Research Office and was accomplished under Cooperative Agreement Number W911NF-18-2-0026. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Office or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein. TEM, XRD, and SEM analyses were performed at the Core Research Facilities (CRF) of Drexel University. The authors thank Tyler Mathis (Drexel) for SEM characterization and assistance with electrochemical device testing of the density gradient electrodes.

**REFERENCES**


