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Functional metal carbide nano structures with unique thermal and electrical chemical properties

Huazhang Zhu
Iowa State University

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Functional metal carbide nano structures with unique thermal and electrical chemical properties

by

Huazhang Zhu

A thesis submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Chemical Engineering

Program of Study Committee:
  Yue Wu, Major Professor
  Zengyi Shao
  Xinwei Wang

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2018

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DEDICATION

In memory of

My Father Zhu, Gaosheng and Mother Zhang, Meiyi
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ABSTRACT

Two-dimensional mxenes, the newly discovered materials have attracted numerous attractions in batteries, super capacitors and electromagnetic screening, etc. Due to the 2D shape and predicted metallic properties of the material, thermal properties of mxenes are expected to be anisotropic and extremely high. To integrate this material into practical devices, gaining insight of its thermal properties will be helpful for the architecture design. However, none of the actual measurements of the materials are yet reported. In regard of the interest, thermal conductivities of bulk Ti$_3$C$_2$T$_x$ mxene prepared by sparking plasma sintering (SPS) technique was measured. The results showed a high anisotropy in thermal conductivities of the material. This study will expedite the material discovery and device optimization of Mxene material in various fields.

This thesis gives an insight on the preparation of Ti$_3$C$_2$T$_x$ mxene flakes and nanostructured Ti$_3$C$_2$T$_x$ mxene disk sample. Thermal conductivity measurement was applied on the obtained disk sample. In this research Ti$_3$C$_2$T$_x$ mxene flakes are obtained from the MAX Phase Ti$_3$AlC$_2$, which is synthesized from Ti, Al, C powders in the stoichiometric ratio of 3: 1.2: 2 at the temperature of 1400°C. SPS was utilized for the MAX Phase preparation and several different MAX Phases were prepared for studying at the beginning of this project. These MAX Phases included Ti$_3$AlC$_2$, Ti$_2$AlC and Zr$_3$Al$_3$C$_5$.

To study the properties of the mxene phase, obtained MAX Phases are grinded into thin powder, thieved through a 325mech screen, and then etched with 48% hydrofluoric acid. To obtain a Mxene Phase disk, mxene flakes are collected after the etching process. Since the surface functional groups have a great impact on the thermal properties of the Mxene phase the collected flakes are soaked in anhydrous hydrazine after washing with DI water.
Hydrazine soaked samples show a quite different thermal property in comparison with the non-soaked samples.

Thermal conductivity of the samples was measured from both the Differential Laser-Heating and Infrared-Imaging (DLI) method and Laser Flash method. The two methods gave similar values on the measurement. The DLI method gives a great illustration on how thermal conductivity of the disk samples can be measured for future relative projects and the behavior of the disk samples shows the anisotropic property of the disks which potentially has many applications.
CHAPTER 1
INTRODUCTION

1.1 Two-dimensional Mxene

Mxene is a phase synthesized from MAX by selective etching of the A element. The Nowotny group first brought out the concept of 3-dimensional transition element carbides/nitrides in 1960s\(^1\). The discovery helped researchers to successfully synthesize phases with similar 3-dimensional structures which then labeled as MAX. Where M is early transition metal, A is group A element and X is C element or N element\(^2\). This category of the phases has a general formula of \(M_{n+1}AX_n\) where n is usually 1, 2 or 3. MAX Phases have a layered hexagonal structure. Since the bonds between M, X elements are mainly covalent and ionic where the bonds between X, A elements are mainly metallic, the A element layer is more active. In 2011, prof. Gogotsi and Prof. Barsoum in Drexel University found out that by selective etching of the MAX phase, a new 2-dimensional transition metal carbide phase can be obtained\(^3\). To emphasize the similarity of the new phase with graphene and the precursor of the material, the 2-dimensional transition metal carbide/nitride phase was named Mxene.

This novel material has a general formula of \(M_{n+1}X_nT_z\)\(^4\), where T is the functional group attached to the surface of Mxene which could be hydroxyl, oxygen, fluorine or other groups. Many Mxene phases have been found which include Ti\(_3\)C\(_2\), Ti\(_3\)CN, Ti\(_2\)C, V\(_2\)C\(_5\), Nb\(_2\)C, Nb\(_4\)C\(_3\), Ta\(_4\)C\(_3\) etc\(^6-8\). The unique characteristics in structure of this new 2-dimensional material endows many special properties to it. Through simulations bare Mxenes are predicted to have a strong metallic and electrochemical property. On top of that, functional groups on Mxene surfaces endows a hydrophilic property\(^6-8\). These properties combined
make the Mxene phase a great candidate for energy storage, hydrogen storage, catalysis and other applications\textsuperscript{9-13}. There also exist band gap transition phenomenon for Mxenes under certain circumstances, optical applications would be another field where the materials have a great potential\textsuperscript{14-17}.

Since the discovery of Mxenes, this new family of materials were well studied with many different purposes. Researched applications such as energy storage devices and catalysts have proved the great potential of this new family of materials\textsuperscript{18-19}. However, the potential application in thermal management of this material is rarely studied. Single layer graphene is proved to have an outstanding thermal conductivity from laser excitation thermal conductivity measurement\textsuperscript{20}. Computational results on mxene flakes show that this family of material has a good thermal property and a strong anisotropy\textsuperscript{21-24}. However, introduction of terminal groups during etching process makes mxenes much less thermally conductive. By treating the mxenes with various methods, different surface chemistry can be obtained\textsuperscript{25-27}. These properties of the material would also have an impact on its thermal conductivity. Researchers have found that interfaces also have a strong impact on thermal conductivity. These features of the material family indicate that mxenes have a great potential in thermal transport applications. Although there is not much report on these applications now, the intrinsic metallic property of this new material will play a part in future research directions. Main challenges like difficulties in synthesis, hazardous chemicals in use and uncontrollable surface terminals are obstructions to further developments of the subject. However, these impediments can be cleared once researchers obtain a better understanding of Mxenes. Ti\textsubscript{3}C\textsubscript{2} as one of the pioneer materials in the Mxene group has been studies the most in the past seven years by Mxene research groups. Hence, our group made further progress into it in the
perspective of thermal property studying. This project was motivated by the high similarity between Ti$_3$C$_2$ and Graphene in structure. The hexagonal thin layer structure and ceramic property of Mxene was a strong indication that this family of metal carbides/nitrides material has a great potential in future applications.

1.2 Bulk Ti$_3$C$_2$T$_x$ disk Preparation

When the Mxene materials were discovered, Hydrofluoric acid (HF) was used as the etching chemical to etch to Al layers in the MAX phases and obtain Mxene phases$^3$. Titanium based Mxenes were the first ones that were found (Ti$_2$CT$_x$ and Ti$_3$C$_2$T$_x$). No much later than that, the idea of enhanced exfoliation and delamination were applied on this family of materials and that gave many new insights to researchers in this area$^{28-32}$. New forms of applications such as transparent Mxene thin films and compressed Mxene clay are generated and many new other applications await.$^{33, 34}$ One perspective of the new insight that our research group gave out was that the delamination of the material provides a better chance for surface modification of the material. For Mxenes that are only etched and washed with DI water, the layered structures obtained are generally stacked together. The layered structures that can be observed are thin layers attached into thinker layers. Access to the surface of the Mxene materials are quite limited while they are firmly stacked. Based on our observation, existence of Fluorine terminal is prevalent for all Ti$_3$C$_2$T$_x$ flake surfaces. After the treatment of anhydrous hydrazine for 24 hours, a large portion of the -F terminals are gone. The surface modification step is where the influence of intercalation and delamination takes in$^{35}$. SEM-EDS results indicated that intercalated Ti$_3$C$_2$T$_x$ flake had a high -F terminal substitution ratio comparing with Ti$_3$C$_2$T$_x$ samples that were not intercalated. Other than hydrazine soaking,
annealing is another method of surface terminal modification. It is reported that annealing helps with removing surface terminal groups of Ti$_3$C$_2$T$_x$ Mxenes to a certain extent, where the bare surfaces can be preserved under vacuum and will be terminated with oxygen groups in air\textsuperscript{36}. Although we do not have any in-situ characterizations for our Sparkling Plasma Sintering setup, the first half of the sintering process highly resembles an annealing process. Where the samples are kept under vacuum and high temperature for a rational time before temperature increases to the actual sintering temperature. During the process the surface terminals like oxygen and hydroxyl functional groups are expected to be removed, yet the roughly 30% of fluorine groups that remained after hydrazine treatment stayed in the bulk sample and had a main impact on the thermal properties of it. During the process, higher temperatures were firstly applied. A sintering temperature as high as 1400\textdegree C was also applied to the material which brought the results of dominating existed TiC. From the phase diagram, it is expected that with an Atomic Percent Carbon of around 40%, TiC is more stable at under temperature over 500\textdegree C. It is not ideal to eliminate the existence of TiC after sintering the disk at a high temperature. However, previous trials over cold pressing on the material were all failed due to the too weak physical properties of the material. After sintering the Ti$_3$C$_2$T$_x$ Mxene flakes into a disk, we used XRD to analyze the sintered disks and found out that TiC was always a portion of the material in all temperature ranges applied. From our analysis the connecting nodes are where the TiC is formed since the morphology of the original multilayer Mxenes are preserved after SPS treatment\textsuperscript{37}. Layered structures were clearly seen along with the structures which resulted from phase transition. The trend was also determined by the location of the material where the centered part of the sample went through a lower temperature sintering and the rest of the sample had a much higher
temperature profile during the sintering process. Further details will be clarified in the following chapter.

1.3 Differential Laser-Heating and Infrared-Imaging

The Differential Laser-Heating and Infrared-Imaging method is based on one dimensional Fourier law. The utilized principle is rather simple, yet the experimental condition is easily affected by many factors and the consistency is hard to maintain in most of the cases. In our setup an infrared camera is used to measure the surface temperature of sintered disks. A laser source heats up the surface of the sample and an aluminum substrate is used for conduction heat transfer which will cool the disks down from the non-heating side. The whole set up is shown in Figure 1.1. The convection heat transfer between surface of samples and air leads to fluctuations on the temperature files of the disk. A whole set up constructed under vacuum would improve the quality of the experiment. However, such a modification will result in many difficulties in operations of the experiment.

Figure 1.1 Photograph of Differential Laser-Heating and Infrared-Imagine Experimental Setup
The optical properties of Ti$_3$C$_2$Tx sintered disk was also an important factor for our experiment. Since Ti$_3$C$_2$Tx has a relatively high optical absorption rate The Differential Laser-Heating and Infrared-Imaging method is ideal for its thermal conductivity measurement\textsuperscript{38}. Besides, the cross-plane and in-plane samples have almost identical surfaces after polishing, which makes it even more rational to use this method. Scanning Electron Microscopy images were obtained for both samples each time before measurement of the thermal properties, it was apparent that each sample were consistent with Mxene flakes perpendicular to the direction of laser source.

To alleviate the influences of the convection heat between measuring samples and surrounding air, we took measurements based on formulated time intervals and increased total number of experimental groups. These measurements were done under room temperature and 8 sets of measured temperature profiles were obtained for each set of experiments. Besides, the obtained thermal conductivities were confirmed with LINSEIS LFA 500 Light Flash Thermal Conductivity measurement setup.

This thermal transport measurement method was certified by measuring many reference materials. The method itself has the advantages of being effective, flexible to physical properties of the material and flexible to sizes of the actual material\textsuperscript{39}. Thickness control was a focal point during the sample preparation process since the disk could only obtained by cutting and polishing the original disk.

1.4 Four-Probe Measurement of Thermal Conductivity

As a side method that we used to certify the thermal conductivity of the material, Four-Probe thermal transport measurement method was also applied in our experiment. By
electrifying the sample is heated and the temperature profile is recorded. This method is in principle similar with the TET method I have discussed in the previous sections. However, this method was applied to on single Ti$_3$C$_2$T$_x$ Mxene layer and brought out a consistent result which is identical with what I obtained from the SPS sintered disk. The method of Four-Probe Measurement has been proved to be highly effective on nanomaterials similar with Mxenes$^{40}$. The seemingly low thermal conductivity is under the impact of fluorine functional groups which gave a quite high contact resistance and made the thermal property measurement quite difficult. The thermal conductivity of the measured values would be lower than the actual values under these circumstances. However, impacts on thermal property of the Mxene samples would be similar with the case of SPS sintered disk. From the SEM spectroscopy we obtained the morphology of the sample measured by Four-Probe Thermal Transport Measurement method. The image showed that the sample had a relatively uniform thickness and a clean surface. However, the sample was still a multilayer structure which resembled the SPS sintered disk. It is extremely hard to obtain absolute single layer mxene even after intercalation or delamination treatment. Thin layer Mxenes claimed by research groups in articles are all mostly few layer Mxenes instead of single layer. The material is expected to be more competitive in the field by the time when single layer Mxenes can be numerous obtained and dominating surface terminals can be controlled in a better way. The results we had from the Four-Probe Thermal Transport Measurement showed that there is a little difference in the thermal conductivity from this sample in comparison with bulk sample. The values measured from the four-probe methods were smaller than the values we had from all the rest of measurements. Contact resistance is a key factor and the
experimental results showed the importance of surface terminals in thermal transport applications.

Figure 1.2 Optical Micrograph of Ti$_3$C$_2$T$_x$ flake on suspended device (Four-probe thermal conductivity measurement method)

1.5 Silicon Nitride Beam Assisted Microfabricated Device

Along with four-probe thermal conductivity measurement method, we were glad that we received more assistance from Prof. Shi Li at University of Texas at Austin to apply more insights on thermal conductivity measurement of thin layer samples. The advantage of this method was to greatly reduce the influence of contact resistance and to obtain a much more accurate value in a much more effective way. In this method, the fabricated device consists of two platinum resistance thermometers, six silicon nitride beams and Pt bonding pads\textsuperscript{41}. Silicon Nitride Membranes are suspended by the beams. Comparing with the four-probe method utilization of the fabricated device eliminated the contact resistance to a large extent
and the result corresponded extremely well with the Differential Laser-Heating and Infrared-Imaging method and Laser Flash Heating Method. The result was another strong convincing factor for the accuracy of our measurements.

![Figure 1.3 SEM Micrograph of Ti$_3$C$_2$Tx flake on microfabricated device](image)

By understanding the differences between these thermal property measurement methods from all different perspectives, we formed our understanding on thermal property measurement of Mxenes. By applying them all on our material, we realized that the silicon nitride beam assisted microfabricated device based method has a great potential on future investigation of thermal transport property of Mxenes.

1.6 Special Thermal Properties of Mxene

In this thesis, I demonstrated that the thermal conductivity measurement of Ti$_3$C$_2$Tx solids prepared by Sparkling Plasma Sintering technique.$^{42}$ To prepare the bulk Ti$_3$C$_2$Tx
material, we used a sintering temperature of 700°C and a sintering pressure of 30MPa. These conditions were obtained based on groups of experiments which brought out compositions of different phases including TiC phase. Detailed characterization data and analysis on obtained results will be provided in Chapter 2. Considering the sintering process leads to a higher temperature in regional areas, it is hard to avoid certain unwanted phases and maintain the conjunctions between the Mxene flakes. This was a main difficulty in the progress of this research and varieties in the sintering conditions had a main impact on the resulting properties of the disk. After the bulk samples were obtained, these samples were measured with the Differential Laser-Heating and Infrared-Imaging method.

Our results clearly showed an anisotropy tendency of the prepared sample. Based on results from our experiments, the in-plane direction thermal conductivity of the bulk sample has a much higher value in comparison with the cross plane one. From the microscopy data I found the general pattern of Ti$_3$C$_2$T$_x$ mxene flakes aligning in the same direction as expected. The alignment was achieved by pressuring from the process of sparking plasma sintering. One thing worth to note is that the results were obtained after modification of surface terminal groups. We foresee that more alternative terminations will bring different thermal properties of the material in the future.
CHAPTER 2
SYNTHESIS OF MXENE FROM MAX AND THERMAL CONDUCTIVITY
MEASUREMENT OF BULK MXENE

2.1 Introduction

The focus of this research is to measure the thermal conductivity of Ti$_3$C$_2$Tx mxene. The original idea of the research was to use excitation laser method to measure single layer Ti$_3$C$_2$Tx mxene with lateral sizes of 5μm\textsuperscript{43}. This method successfully obtained the thermal conductivity of Single-Layer Graphene (SLG). However, unlike SLG, the characteristic peaks of this material under micro-Raman spectroscopy is not strong enough to generate an analytical result\textsuperscript{44}. One different method we tried to measure thermal conductivities was the Transient Electrothermal Technique (TET) method\textsuperscript{45}. One-dimensional wire shaped samples were made and secured on two electrodes and electrified. From the heat generated we can obtain the thermal properties from combining the transient temperature response and steady-state temperature response. However, the high electrical conductivity of the sample made it difficult to get good responses over noise generated by the system. With experimental methods not suitable for our sample, we then chose to obtain results from bulk solid of Ti$_3$C$_2$Tx with Differential Laser-Heating and Infrared-Imaging Method.

Simulation based calculations showed that two-dimensional Zirconium and Hafnium carbides have a strong thermal diffusion property and are great candidates for such applications\textsuperscript{22}. Some of the research groups have successfully utilized the Chemical Vapor Deposition (CVD) method to grow two-dimensional Tungsten carbide\textsuperscript{46}. One drawback that this method has is the obstruction towards industrial purposes. Only an extremely limited
amount of the material can be synthesized from each batch with this method. The benefit of the CVD method is a better control over the synthesizing conditions and the guaranteed higher quality and consistency of final products. Basic research on novel materials usually require more consistent outcomes from samples. The CVD method will be a great perspective for researchers to acquire in-depth knowledges of this family of new materials. Considering all the impediments we encountered during the process of measuring single flake Mxenes and micro-sized samples, we bypassed the route and research Mxenes’ thermal properties through bulk samples instead. Here we provided a measurement of the bulk material thermal properties, where some features of the material were shown through the form of bulk sample.

2.2 Mxenes Synthesis Method and Sample Preparation Method

2.2.1 Materials

Titanium Powder (Ti, ≥ 99.98%), Aluminum Powder (Al, ≥ 99.5%), Zirconium Powder (Zr, ≥ 99.5%), Hydrofluoric Acid (HF, ≥ 49%) and Anhydrous Hydrazine (N₂H₄, ≥ 98%) were purchased from Sigma Aldrich, Graphite Powder (Graphite, ≥ 99%) was purchased from Alfa Aesar. Reagent alcohol (EtOH, ≥99%) was purchased from VWR.

2.2.2 Synthesis of Ti₃AlC₂ MAX Phase powder

The Ti₃AlC₂ MAX was synthesized from titanium powder (Aldrich, 99.98), aluminum powder (Aldrich, 99.5) and graphite powder (Alfa Aesar, 99%) with a molar ratio of 3:1:2. The powder mixture was sintered in a graphite die at a temperature of 1400° C for 1hr. 3g of the powder mixture was used for each synthesis. During the process, a 30MPa pressure was applied on the graphite punch and the temperature was controlled to increase by
50° C per minute from RT to 1400° C. This method was well studied for synthesis of Ti$_3$AlC$_2$ MAX. [10] After sintering, a Ti$_3$AlC$_2$ disk is obtained and is cooled down to RT by water cooling system of the SPS. The disk was then grinded with mortar and pestle then filtered through a 325mesh sieve. The resulting powder is Ti$_3$AlC$_2$ powder with size of smaller than 44μm. The morphology of the MAX powder clearly shows a layered structure before any chemical treatment.

![Figure 2.1 Schematic of Sparking Plasma Sintering(SPS) System](image)

**Figure 2.1 Schematic of Sparking Plasma Sintering(SPS) System**

### 2.2.3 Synthesis of Zr$_3$Al$_3$C$_5$ MAX Phase powder

The Zr$_3$Al$_3$C$_5$ MAX was synthesized from Zirconium powder (Aldrich, 99.5), aluminum powder (Aldrich, 99.5) and graphite powder (Alfa Aesar, 99%) with a molar ratio
of 3:4.2:5. The powder mixture was sintered in a graphite die at a temperature of 1900° C for 1hr. 3g of the powder mixture was used for each synthesis. During the process, a 30MPa pressure was applied on the graphite punch and the temperature was controlled to increase by 50° C per minute from RT to 1900° C. After sintering, a Zr$_3$Al$_3$C$_5$ disk is obtained and is cooled down to RT by water cooling system of the SPS. The disk was then grinded with mortar and pestle then filtered through a 325mesh sieve. The resulting powder is Zr$_3$Al$_3$C$_5$ powder with size of smaller than 44μm.

### 2.2.4 Synthesis of Ti$_3$C$_2$Tx Mxene powder.

Ti$_3$C$_2$Tx mxene flakes were obtained from etching of Ti$_3$AlC$_2$ MAX Phase power with 49% percent HF. 2g of the powder received from the previous step was weighted and mixed with 20mL of HF at RT. The mixture was stirred with assistance of a Teflon magnetic bar which was stirring at 200rpm. The reaction was under RT for 24hr. After reaction, the mixture was centrifuged out from HF at 8900rpm for 2hr. The product was then washed ~10 times with DI water till the pH of the water/Mxene mixture has a pH of ~7.

### 2.2.5 Synthesis of Zr$_3$Al$_2$Tx Mxene powder.

Zr$_3$Al$_2$C$_5$ mxene flakes were obtained from etching of Zr$_3$Al$_3$C$_5$ MAX Phase power with 49% percent HF. 2g of the powder received from the previous step was weighted and mixed with 20mL of HF at RT. The mixture was stirred with assistance of a Teflon magnetic bar which was stirring at 200rpm. The reaction was under RT for 48hr. After reaction, the mixture was centrifuged out from HF at 8900rpm for 2hr. The product was then washed ~10 times with DI water till the pH of the water/Mxene mixture has a pH of ~7.

### 2.2.6 Preparation of termination modified Ti$_3$C$_2$Tx Mxene powder.
2g of mxene powder obtained from the previous step was collected and mixed with anhydrous hydrazine (Aldrich). The mixture was then kept under RT for 24hr with 200rpm stirring. After 24hr of mixing, the product was centrifuged out from anhydrous hydrazine with 1hr centrifugation at 8900rpm. Then collected material was washed with DI water for ~5 times to wash out the anhydrous hydrazine. 20mL of DI water was added after washing the product. The solution was bath sonicated for 6hr to make a suspension. The suspension was collected and centrifuged at 3500rpm for 30 min to remove any possible impurities introduced from the synthesis stage and Ti$_3$AlC$_2$ residues that were introduced from the etching process. After this step, the resulting mixture consist of mostly thin layer Ti$_3$C$_2$Tx mxene flakes. The product was then washed with ethanol and centrifuged out to dry under vacuum. After 24hr of drying under vacuum powder consists mostly Ti$_3$C$_2$Tx thin flakes is prepared.

2.2.7 Preparation of Ti$_3$C$_2$Tx Thermal Conductivity Testing Mxene Samples.

2g Ti$_3$C$_2$Tx mxene flakes powder collected from the previous step was then fitted into a 10mm graphite die to sinter. A 40MPa pressure is applied onto the powder and the powder is sintered at 700°C for 30 minutes. A temperature increasing rate of 50°C was used and the product was cooled down to RT after sintering. With any higher temperature applied for sintering the resulting product was consisted of mainly TiC. After cooling down, the disk was cut with a wire saw into in-plane direction and cross-plane direction square shape disks. The disks were then used for infrared laser heating testing.

2.2.8 Preparation of Ti$_3$C$_2$Tx/PDMS composite Testing Samples

0.2g Ti$_3$C$_2$Tx mxene flakes powder prepared and dried was mixed with 1g of monomer PDMS base. The mixture was stirred under RT for 24hr and then bath sonicated for
6hr. 0.1g of curing agent was then added to the mixture and stirred under RT for another 24hr. The product from mixed components were then heated under vacuum at 75°C for 12hr. The procedures were repeated for pure PDMS disk sample without addition of Ti$_3$C$_2$Tx mxene flakes. Both samples were collected after the curing process was done.

2.3 Characterization of the obtained materials

The crystal structure and composition of Ti$_3$AlC$_2$ MAX, Ti$_3$C$_2$Tx mxene powder and sintered Ti$_3$C$_2$Tx mxene disk were analyzed on a Siemens D500 x-ray diffractometer which has a Cu Kα source. The surface morphology of the testing samples was analyzed by a FEI Quanta 250 FE-SEM. Surface of Ti$_3$C$_2$Tx mxene disk was polished before spectating with SEM. The microscope image of PDMS/ Ti$_3$C$_2$Tx mxene composite was taken with Olympus optical microscope. After the etching process and treatment of anhydrous hydrazine, Ti$_3$C$_2$Tx mxene flakes were observed under low magnification TEM. The thin layer structure was confirmed with TEM imaging. This was achieved with JEOL 2100 TEM under the acceleration voltage of 200kV.

Except for the newly prepared Ti$_3$C$_2$Tx samples, all samples were analyzed with XRD as a bulk material. Ti$_3$C$_2$Tx powder is analyzed with Siemens D500 x-ray diffractometer as powder. Since the powder was washed many times with DI water and dried after washing with alcohol, the powder itself was not hazardous and did not need any special treatment in the analyzing process. Powder samples were compressed on a 3cm diameter sample holder, bulk samples were simply secured with plasticine.

Transmission Electron Microscopy samples were prepared by slowly dipping 8 to 10 drops of diluted solution of Mxenes onto a 200mesh Lacey TEM id. To avoid conjugation of
materials and improve the quality of the images taken, the Ti$_3$C$_2$T$_x$ samples were firstly obtained by washing with ethanol, then dispersed in the ratio of about 1g to 90mL. A small portion of the material is then taken and diluted to about 180 times to obtain thin solutions of Ti$_3$C$_2$T$_x$ Mxene. Then the dipping process made good scattered sampled on TEM grid and made the thin layer Mxene easy to be observed.

SEM imaging played a really important role in this project. The morphology of the material under a certain step was a quite important basis for analyzing the composition of the material and the influence of the treating methods. Strong indications like visible anisotropy in sintered disk and formation of porous structure after high temperature sintering constructed our understanding to the etching process and sintering process. EDS analysis was a good basic determination of surface terminations. Through the atomic ratio between titanium and fluorine on the surfaces of the Mxene materials we could get a general idea of the composition of surface terminations and give out our best effort to analyze their impact on thermal transport property.

2.3.1 XRD analysis on samples by preparation methods

From the XRD analysis, the composition of Ti$_3$AlC$_2$ MAX, Ti$_3$C$_2$T$_x$ Mxene and the Ti$_3$C$_2$T$_x$ Mxene sintered disk is certified. The Ti$_3$AlC$_2$ contains Ti$_3$AlC$_2$ with minor Ti$_2$C$_{0.06}$ phase. Figure 2.2 shows the XRD analysis of sintered Ti$_3$AlC$_2$ MAX. Where all labeled peaks correspond to Ti$_3$AlC$_2$ MAX and the unlabeled peaks at roughly 41 and 45 corresponds to Ti$_2$C$_{0.06}$. XRD data was obtained from both the bulk sintered material and grinded powder. The one shown was from sintered bulk Ti$_3$AlC$_2$ MAX Figure 2.2(a).
Figure 2.2 (a) XRD Pattern of SPS sintered Ti$_3$AlC$_2$ MAX at 1400° C

Figure 2.2 (b) XRD Pattern of HF etched Ti$_3$C$_2$Tx

Figure 2.2 (c) XRD Pattern of bulk Ti$_3$C$_2$Tx disk sintered at 700° C
After etching with hydrofluoric acid, the composition of obtained substance is complicated due to several reasons. First, although researchers have studies the mechanism of etching process from many perspectives, the reaction is extremely hard to monitor due to the existence of hazardous HF\textsuperscript{47}. Also, during the washing process the product is always collected selectively since the supernatant from centrifugation process always contain a large portion of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} Mxene. The composition of Ti\textsubscript{3}AlC\textsubscript{2} MAX is also an uncertainty. Uniformity of the Ti, Al, C powder in the synthesis process is not easy to control and contract area with surrounding carbon could also lead to composition reaction of TiC and other Ti-C based substances.

For safety reasons, Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} Mxene obtained from the previous step was washed about ten times to bring its PH back to around 7. During the washing and centrifugation process a large portion of the material is lost with the process of pouring the supernatant. Thus, only a small portion of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} Mxene is preserved from each batch of synthesis. The XRD analysis was based on the small portion of the powdered material and the intensity is quite weak comparing with the bulk materials. However, the unexpected substances are under the range of showing an intensity on XRD analysis. The peaks corresponded well with previously obtained results by other research groups\textsuperscript{48}.

To ensure the purity of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} Mxene and improve the accuracy of our measurement, we had more centrifugation steps in between the washing step and the hydrazine soaking step. Dispersed Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} Mxene flakes were centrifuged at 3600RPM for 5 min to get rid of the Ti-C impurities that were introduced into system by Ti\textsubscript{3}AlC\textsubscript{2} MAX synthesis step. Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} Mxene flakes were then collected and soaked with anhydrous
hydrazine. The XRD pattern in Figure 2.3 (b) was from the Ti₃C₂Tₓ Mxene flakes prior to hydrazine soaking.

After soaking with hydrazine Ti₃C₂Tₓ Mxene flakes were then washed with ethanol and dried under vacuum. Detailed steps were illustrated in previous sections. After the powder is dry the material was fitted into a graphite die and sintered under SPS. As previously illustrated TiC is expected based on phase diagram. However, it turns out that TiC is not the only impurity that appeared. The XRD Pattern showed that a small portion of Ti₃AlC₂ was also part of the system. Although SEM EDS analysis from the previous section also showed the existence of Aluminum element in the system, the aluminum signal could be from aluminum fluoride which was formed during the etching process. Again, this result is a convincing indication of the incomplete etching process. After sintering the denser bulk material resulted a stronger intensity for the XRD analysis and the Ti₃AlC₂ signal can then appear from the XRD pattern. Reactions between Ti₃AlC₂ and HF only gives a partial etching process and many of the thin layer Mxenes still have their Aluminum layers preserved. This is also part of the reason why Mxene flakes are amenable to intercalation and delamination in some cases. The unthorough reaction is one of the issues need to be addressed in the future.

TiC is simply an unavoidable impurity that is introduced into the system during sintering process. By not reaching the sintering temperature of 700°C the flakes are not jointed. The resulting disk is too vulnerable for further experiments. From the XRD pattern we realized that Ti₃C₂Tₓ Mxene flakes were partially transferred into TiC by the sintering process. We expected an obvious change in morphology of the material as well. Characterization on morphology would be quite important for further determination of the impacts of this sintering process. Ti₃C₂Tₓ is still the dominating phase in the system, yet the
composition of the substances has definitely been changed during the sintering process. The detailed morphology analysis of the same sample is in the following section.

2.3.2 SEM Analysis on Ti$_3$AlC$_2$ MAX and treated Ti$_3$C$_2$T$_x$ mxene

The SEM analysis of material is all started from the Ti$_3$AlC$_2$ MAX which had the layered structure observed even before treatment of any chemicals (Fig. 2.3, (a)). Interestingly, the Ti$_3$AlC$_2$ MAX grinded sample had some exfoliation phenomenon after physical treatment with agate mortar and pestle. From the SEM micrograph we can clearly see that there is some peeling phenomenon over the surface of the material. Although the main method of getting the Mxene material is utilizing hydrofluoric acid to etch the aluminum layer off from the lattice structure, it is not entirely determined that there is no other method of obtaining 2-dimensional material from the parent MAX structure. Other than that, it is clear from the same image that the fracture surface has a layered shape morphology. The morphology is always, to a certain extent, preserved after the etching process. Some research groups have tried to utilize intercalation, delamination methods such as PDMS and LiF helped treatments to further break down the layered morphology and obtain single layer structure$^{28}$. However, acquisition of single layer or few layer Mxene material is still a challenge. From the first SEM micrograph we have an indication that physical treatment does have an impact on the exfoliation process without effort as strong as the chemical method which is HF etching. It is seemingly possible that a chemical method combined with physical treatment could improve the exfoliation process$^{49}$, liquid assisted grinding, for instance, would be worth to try for future researches. Substitution of highly hazardous hydrofluoric acid shall be one of the priorities in research of MAX/Mxene.
Figure 2.3 (b) showed the Ti$_3$C$_2$T$_x$ mxene flakes obtained from HF etching and treatment with anhydrous hydrazine. One common thing for all the samples prepared with all different intercalation or delamination conditions was that they all partially consisted with multilayer Mxenes. It is extremely hard to separate them from few layer Mxene flakes which were much thinner. The novel preparation method of Titanium Carbide ‘Clay’ brought out by Prof. Yury Gogotsi & Michel W. Barsoum in 2014 made it possible to obtain single layer and double layer Mxenes$^{34}$. With similar intercalation methods we had uniformly thin layer Mxenes obtained. From many of the SEM micrographs taken we found that the process of etching and hydrazine treatment delivered us loosely stacked Mxene flakes. More characterization data on the material will also be provided in the section of Transmission Electron Microscopy.

SEM images of sintered Ti$_3$C$_2$T$_x$ Mxene disks also provided enormous information on the sintered bulk Ti$_3$C$_2$T$_x$ Mxene sample. Clearly the original morphology was preserved for the samples and this phenomenon was prevalent for all the samples that I had sintered at different temperature ranges. Difference between the sintered disks was concentrated upon formation of TiC for different temperature ranges. Although the alignment was not perfect for all of them there was a strong visible trend that the Mxene flakes would align with the in-plane direction of the sintered disk as shown in (Fig. 2.3, (c)). This anisotropy in morphology lead to an anisotropy of thermal transport property which will be shown in following sections. Ti$_3$C$_2$T$_x$ Mxene flakes were integrated and compressed after the SPS treatment.
Figure 2.3 SEM Micrograph of a) Grinded Ti$_3$AlC$_2$ MAX, b) HF etched and hydrazine soaked Ti$_3$C$_2$Tx Mxene, c) SPS sintered Ti$_3$C$_2$Tx Mxene at 700° C

The SEM EDS was a powerful tool for surface termination analysis. By comparing the atomic ratio between fluorine and titanium element it is obvious that a large portion of fluorine terminal groups have been eliminated by the hydrazine treatment process (~67%). This result was repeatable and consistent for all the hydrazine treated Ti$_3$C$_2$Tx Mxene samples. The EDS spectrum in Figure 2.4 was one of the previously obtained results.

Figure 2.4 SEM EDS Spectrum of Ti$_3$C$_2$Tx mxene prior and after Hydrazine Soaking
2.3.3 TEM Analysis on Ti$_3$C$_2$T$_x$ mxenes

Characterization images under TEM was not only used for confirming the material by analyzing the lattice structure. TEM microscopy was also a main method for us to determine the lateral sizes of the 2-dimensional material. On top of that, we found some features of Ti$_3$C$_2$T$_x$ mxene flakes that were predicted by other research groups from simulation.

Firstly, the lattice constant of the hexagonal structure of synthesized material was 3.03Å from FFT analysis which corresponded well with Ti3C2 Mxene phase and the featured few layer structure was determined. From the TEM Image the few layer structures were clearly visible on Lacey TEM grids and the lateral size obtained from our synthesis method was large in comparison with flakes obtained by other research groups who applied similar practices. It was our original intention of our experiments was to acquire Mxene flakes with large lateral sizes and fit it onto methods such as four-probe and six beam fabricated device to measure its thermal conductivity. Through investigation of etching condition, intercalation condition and centrifugation condition we developed a reliable procedure of making Ti$_3$C$_2$T$_x$ mxene flakes with relatively large lateral sizes.

Through the investigation process we found some interesting phenomenon that were predicted by MAX/Mxene research groups. By varying the sonication conditions, the flakes obtained had some transitions in morphology. Sonicating the material with a relatively long time with bath sonication results in folded or curled thin Mxene flakes (Figure 2.5 (b)). The phenomenon indicates that the material has a quite flexible physical property and is not easy to break.

In Figure 2.5 c, the HRTEM Image shows a few layer Ti$_3$C$_2$T$_x$ mxene flake under the inspection of TEM. Lattices are clearly shown. This novel material had its nanocrystalline
structure determined for the first time in 2014. Mxene flakes’ existence as nanomaterial made it hard for traditional crystallography characterization methods to analyze the material thus the availability of crystalline analysis is quite limited. The characterized Mxene flake samples all had a common feature of easily observed lattices with only thin layers. This indicated that the mxene flakes obtained from the etching of MAX had a strong anisotropy themselves. The lateral sizes of Mxene flakes were mostly between 3μm and 6μm. Under these conditions, the synthesized Ti₃C₂Tx mxene flakes were first characterized with TEM and then fitted onto devices for thermal conductivity measurements. For both four probes method and six beam fabricated device method mentioned in previous sections, the nanoflakes were first prepared, then characterized with TEM on Lacey grids, can lastly located on sample grids for convenience of further experiments.

![Figure 2.5 TEM Micrograph](image) Figure 2.5 TEM Micrograph of a) HF etched Ti₃C₂Tx mxene sample, b) Ti₃C₂Tx mxene sample after hydrazine soaking and bath sonication, c) Ti₃C₂Tx mxene sample at high resolution

2.4 Thermal Transport Property Measurements

Since the discovery of this novel material none of any thermal transport properties of any Mxene was ever reported by any group. The strong metallic and electric properties of
this material made us wonder its potential on thermal transport applications. Research groups specializing on simulations have made some predictions on the thermal transport performance of the material and have measured the electrical properties of some cold-pressed bulk Mxene materials.\textsuperscript{50} The highly hazardous synthesis process is only one limitation to the motivation of the research groups, it is not a coincidence that researchers have not gained much progress on physical property measurement of this material. Challenges that I encountered during the process of thermal conductivity measurement of Mxene flakes are, indeed, what future researchers in the same direction want to overcome.

Mxenes are nanomaterials which has a synthesis process and collection process that is hard to control. Many of the key features like lateral size, surface terminals, layer numbers are usually inconsistent. Mxenes could potentially be metallic two-dimensional materials with no functional groups attached on surface, yet what researchers can study are consistently Mxene flakes with fluorine, oxygen and hydroxyl surface terminals. Terminal groups can be eliminated by annealing under ideal conditions, yet the terminals would reattach to the surface of the material in air. Surface terminalized Mxenes are semi-conducting and their properties are changed enormously\textsuperscript{51}. It is not easy to study the intrinsic properties of the Mxene material.

Lateral size of the material is another difficulty on progressing into thermal transport property measurement of this material. Fabricated devices are required under the scale of nanometer and the lateral size of Mxene flakes are much smaller comparing with materials such as graphene or carbon nanotubes. Contact resistance is the main challenge in thermal conductivity measurement experiments and Mxene materials usually have a large contact resistance due to its inconsistency in shape and surface terminals\textsuperscript{52}. Although cold pressed
samples were successfully prepared and tested by researchers, the contacts between Mxene flakes determined that the results were not a good enough indication for the intrinsic properties of the material.

Combining these feature of Mxene flakes we still decided to try all the possible methods for measurement of thermal transport property of Ti$_3$C$_2$T$_x$ mxene. Our exploration would be a solid step toward a better understanding of this new material with great potential.

2.4.1 Differential Laser-Heating and Infrared-Imaging Method

The Differential Laser-Heating and Infrared-Imaging system consists of one infrared camera that detects the surface temperature of the sample, one laser source that heats up the sample and one sample substrate where the sample is secured. The sample substrate is an aluminum block that is much larger in size comparing with the testing samples. Each mxene disk was firstly secured on the aluminum block, tested with the set up and then tested with addition of glass. To obtain the analytical data, the temperature change of the sample surface was recorded by the infrared camera. A designated area is used as the data source for the calculations. The designated area was selected as the surface of testing sample, which is located at the center of the projected laser source. The testing sample was secured with silver paste which provides a great contact. For the first step of the testing, the sample is secured on the aluminum substrate with silver paste. For the second, the square glass is firstly secured on the aluminum substrate, then the sample is stick onto the glass with silver paste. Silver paste covers the whole interface and excess silver is cleaned to avoid undeserved thermal diffusion. Each set of tests begins with the stabled starting temperature measured from the testing
sample surface, then the laser is projected on the surface and the temperature is recorded after ~ 5 min to let the temperature increase and stabilize.

![Diagram](image)

**Figure 2.6** (a) Schematic illusion of cross-plane and in-plane sample preparation method (b) Photograph of dimensions of sintered disks

Figure 2.6 (a) shows the schematic illusion of how the in-plane Ti$_3$C$_2$T$_x$ mxene sample and the cross-plane Ti$_3$C$_2$T$_x$ mxene were prepared. After cutting the disk by corresponding direction with a wire saw, the resulting disks were fitted on sample substrate for thermal conductivity measurement. The heat conduction from sample surface to the aluminum block was used to analyze the thermal conductivity of the samples. Since the aluminum block is much larger in size comparing with the samples prepared. As a substrate, the thermal conduction affected by aluminum block was neglected. As the conduction and contact enhancement between substrate and sample, the silver paste was assumed to have perfect heat conduction. The two testing conditions and testing images are shown in figure 2.7.
The Fourier law of heat conduction was applied during the calculation of the thermal conductivity\textsuperscript{53}. To reduce possible errors introduced in this process, a designated spot on aluminum substrate was labeled and used for all thermal conductivity measurement. Heat diffusion with surrounding atmosphere is neglected. At the beginning of the measurement, sample on substrate is tested with the setup where

\[
\varepsilon Q_1 = \frac{\Delta T}{R_1 + R_{\text{sub}}} = \frac{T_1 - T_0}{R_1 + R_{\text{sub}}} \quad (2.4.1)
\]

The corresponding testing sample surface temperature under laser heating $T_1$ and the end surface temperature $T_0$ are both determined by infrared camera. $T_0$ is firstly determined at RT. Then a constant laser source is projected to cover the surface of the sample where the sample is at the center of the laser spot. After ~ 5min the surface temperature of the testing sample remains stable when $T_1$ is recorded. The procedure repeats 4 times and
four sets of $T_1$ and $T_0$ values are obtained. Then the testing sample is cleaned and applied on the substrate with the addition of the glass piece. The glass piece covers exact the same area on substrate as the surface area of the testing sample. The new testing sample surface temperature under laser heating $T_2$ and the end surface temperature $T_0$ are again both determined by infrared camera. In this step sample is tested with the setup where

$$
\varepsilon Q_2 = \frac{\Delta T}{R_1 + R_{glass} + R_{sub}} = \frac{T_2 - T_0}{R_1 + R_{glass} + R_{sub}} \tag{2.4.2}
$$

Since the laser heating was applied on the same surface of the testing sample with the same laser power from the same distance,

$$
\varepsilon Q_1 = \varepsilon Q_2 \tag{2.4.3}
$$

Then,

$$
\frac{T_1 - T_0}{T_2 - T_0} = \frac{R_1 + R_{sub}}{R_1 + R_{glass} + R_{sub}} \tag{2.4.4}
$$

With thermal resistance of testing sample $R_1$, thermal resistance of glass $R_2$ both determined from the corresponding thickness, surface area and thermal conductivity, thermal conductivity $k_1$ can then be calculated.

$$
R_1 = \frac{d_1}{Ak_1}, \quad R_{glass} = \frac{d_{glass}}{Ak_{glass}} \tag{2.4.5}
$$

In the process of the experiments we found that the terminal groups of Ti$_3$C$_2$T$_x$ mxene has a crucial impact on the thermal conductivity of the obtained Ti$_3$C$_2$T$_x$ disk. Without the treatment of hydrazine anhydrous the obtained results were much lower than the results presented. However, anhydrous hydrazine only partially illuminates hydroxyl and fluoride terminal groups$^{54}$. Although the treatment also helps with removing the water content, the interface between the Ti$_3$C$_2$T$_x$ flakes still plays an essential role on the thermal conductivity of the testing samples.
Other than surface treatment, delamination of the Ti$_3$C$_2$Tx powder prior to sintering and testing was also done yet the results did not show any obvious difference. Although the delamination process could lead to fully separated thin flakes, the surface chemistry of fully delaminated sample is quite similar with regular samples prepared as illustrated. [17] It was found that a delamination process does not help with getting more terminal groups replaced from the EDS analysis under SEM. Thermal properties of the bulk sample prepared from the SPS process did not depend much on how delaminated the material was.

The thermal conductivity of in-plane direction of the disk was evaluated to be 2.55 W/(mK) and the thermal conductivity of cross-plane direction of the disk was evaluated to be 1.94 W/(mK). These values show that an anisotropic trend exists in a Ti$_3$C$_2$Tx samples after sintering. These values were then confirmed with Linseis LFA 500 light flash thermal conductivity measurement system.

### 2.4.2 Silicon Nitride Beam Assisted Microfabricated Device Method

In this method a few layer Ti$_3$C$_2$Tx mxene flake was suspended on the fabricated device and the whole setup was placed under vacuum. The fabricated device consists of one heating unit and one sensing unit. Both are Silicon Nitride membranes as illustrated in Chapter 1. One Platinum Resistance Thermometer (PRT) is connecting with each membrane by contact pads. The heating PRT is electrified with dc current and the heat is the conducted to the sensing unit through measured sample. Air conduction and radiation is negligible in the system, detailed experimental conditions can be found in reference literatures. The general principle is that the thermal conductance of sample, $G_s$ can be found from energy conservation in the fabricated device system.
\[ G_s = G_p \frac{\Delta T_s}{\Delta T_h - \Delta T_s} \quad (2.4.6) \]

Where \( G_b \) is the total thermal conductance of the beams, \( \Delta T_s \) is the temperature change of sample and \( \Delta T_h \) is the temperature change of heating PRT. By applying the same energy conservation, the total thermal conductance of the beams can be obtained from the following equation.

\[ G_B = \frac{Q_h + Q_L}{\Delta T_h - \Delta T_s} \quad (2.4.7) \]

Values of heat generation from PRT unit \( Q_h \) and heat generation from Pt leads \( Q_L \) are calculated based on dc current settings. From the resistances obtained from two PRTs, \( \Delta T_h \) and \( \Delta T_s \) are calculated. Once the thermal conductance is obtained, lateral sizes and thickness of the material is measured and the thermal conductivity, \( k \) is calculated from the equation of thermal conductance.

\[ G_s = \frac{k_s A_s}{L_s} \quad (2.4.8) \]

Here the contact resistance is neglected. Extra metal was deposited near joint points between the sample and device. The impact of contact resistance was minimized in this experiment. Image of Ti\(_3\)C\(_2\)Tx few layer Mxene is shown in Figure 2.8.

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Figure 2.8 SEM micrograph of Ti\(_3\)C\(_2\)Tx flake secured on Microfabricated Device
Thermal conductivity of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> flake is measured to be ~ 1.58 at RT and 1.8 at around 400K. The main source of error under the experimental circumstance is still the neglected contact resistance. In comparison with bulk disk thermal conductivity values measure from the Differential Laser-Heating and Infrared-Imaging Method, these values were expected to be lower. Existence of Ti-C phases in the sintered bulk disk would also increase the thermal transport properties and deviate the measured values from its intrinsic property. In thermal conductivity measurement experiments errors are always influential. Results obtained from these methods were evident for us to illustrate that thermal conductivity of this novel material lies with in this range due to effects of terminal groups and crystalline distribution features which awaits further discovery.

Figure 2.9 Thermal Conductivity Measurement results from Silicon Nitride Beam Assisted Microfabricated Device

2.4.3 Thermal Conductivity Measurement on Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>/PDMS composite

Applications of materials with special thermal transport properties composited with polymers like PDMS (polydimethylsiloxane) and PMMA (polymethylmethacrylate) have always been a focus of material based researches since tuning of thermal properties can be achieved through composition<sup>55, 56</sup>. Polymers are widely used in devices, characteristics like flexibility and internal mobility are important for special applications. During the research
process we also found interesting changes of physical properties after PDMS is composited with Ti$_3$C$_2$T$_x$, in this thesis only changes in thermal transport properties are emphasized.

The original intention of this project was to form a Ti$_3$C$_2$T$_x$ Mxene network within the PDMS composite. To achieve the objective, Mxene powder was well mixed with silicone elastomer by magnetic stir bar assisted stirring and bath sonication before Sylgard 184 curing agent was added. Detailed experimental conditions were explained in section 2.2.8. Synthesis process of the disks were identical except for the addition of Ti$_3$C$_2$T$_x$ Mxene within the composite sample. Resulting sample had a uniform color and the distribution of Ti$_3$C$_2$T$_x$ Mxene flakes was analyzed through Optical Microscopy.

Mixing conditions were found to be crucial for the homogeneity of the resulting sample. Without a long time of bath sonication, the uniformity of the resulting sample was not as good. Properties were inconsistent from sample to sample. A 2-hour stirring followed by a 24-hour bath sonication resulted in a decently mixed sample. From the examination with Optical Microscopy, it was shown that the mixing method was quite effective. Preparation methods, resulted samples and microscopy images are shown in Figure 2.10. Both the composite and pure PDMS samples were cut into disks with uniform thickness and then tested with Differential Laser-Heating and Infrared-Imaging Method the same way Ti$_3$C$_2$T$_x$ Mxene bulk samples were tested.
Figure 2.10 a) Schematic Illustration of PDMS/Ti3C2Tx composite preparation and pure PDMS preparation. b) Photo Image of PDMS/Ti3C2Tx composite & pure PDMS. c) Microscope image of PDMS/Ti3C2Tx composite showing homogeneity of Ti3C2Tx in composite.

In comparison with pure PDMS, PDMS/Ti3C2Tx composite showed an enhancement of thermal conductivity from 0.2502 W/(mK) to 0.3220 W/(mK) at RT. Thermal conductivity of Ti3C2Tx/PDMS composite showed a fair improvement in thermal conductivity in comparison with pure PDMS, which illustrates that this family of materials can be used to tune thermal properties of polymers as a blending composite. The mxene flakes were uniformly distributed in PDMS as shown in the photo image. The improvement in thermal property was quite limited for the case. A better way for the surface treatment of the material shall be researched to further enhancement the thermal property of mxenes.

2.4.4 Light Flash Analysis Method

Differential Laser-Heating and Infrared-Imaging Method is not the only method we tried on our samples. With the assistance of Linseis LFA 500 Thermal Conductivity / Diffusivity measurement equipment available in our research lab we could use the Light Flash Analysis Method to measure the thermal conductivity of bulk Mxene disks. The advantage of this method is that the thermal transport properties of specimen can be measured at an elevated temperature\(^57\). During the measurement process, an intense light is shot on the bottom surface
of the bulk disk and the light absorbed by the surface results in a temperature increase. A high-speed IR detector records the temperature profile of the top surface. The temperature versus time profile is then analyzed to obtain the thermal diffusivity of the bulk disk. Thermal conductivity of the bulk disk was calculated based on the obtained thermal diffusivity values (Figure 2.11).

![Figure 2.11 Thermal Conductivity of Ti₃C₂Tx Mxene bulk in cross-plane direction vs. in-plane direction](image)

In section 2.4.1, it was shown that there was a notable difference between two samples’ thermal conductivities while measured at RT with Differential Laser-Heating and Infrared-Imaging Method. The Thermal Conductivities measured from LFA 500 system showed the same trend. It is apparent that In-Plane Thermal Conductivities values are generally higher than Cross-Plane Thermal Conductivity values for Ti₃C₂Tx Mxene bulk disk. The anisotropy property of the bulk disk material is displayed through its thermal transport properties.

2.4.5 Electrical Conductivity Measurement of Synthesized Phases

By the time we had an initiation of this project, we started from measuring the electrical properties of the new MAX material after successful synthesis. It was found before
we focused on the thermal properties of the material that the MAX phase has a strong metallic property. The discovery of Mxene was from the etching process of hot pressed samples and Sparking Plasma Sintering was a relatively new method for MAX synthesis. Some research groups have reported synthesis of Si based MAX phases and some had ever considered the possible anisotropy existed in the MAX phase\(^{58}\). From our research groups’ experience generated pulse from the sintering process has a strong impact on the direction of growth of lattice and location of phase transition under high current. From electron conductivity measurement we noticed an obvious anisotropy in SPS sintered MAX materials.

![Graph](image)

**Figure 2.12** Electrical Conductivity of SPS sintered Ti\(_2\)AlC MAX bulk in cross-plane direction vs. in-plane direction

One way to explain the resulted anisotropy would be that the lattice growth direction is influenced by direction of current and generated magnetic field in Sparkling Plasma Sintering. As we have shown in previous sections, MAX phases have a layered structure and the physical properties comply with the anisotropy of the material. The Ti\(_2\)AlC MAX phase we analyzed had a strong metallic property like most of the Al based MAX phases, thus the electrical conductivity decreases as temperature increases. Measured electrical conductivities
in two directions showed that the in-plane direction disk specimen has a much higher electrical conductivity than the cross-plane direction disk as in Figure 2.12.

In the case of sintered Ti$_3$C$_2$T$_x$ Mxene bulk disk electrical conductivities measurement results showed different features. The values of electrical conductivities from in-plane and cross-plane disks were within the same range yet for the in-plane disk thermal conductivity decreases as temperature increases and vice versa for the cross-plane disk as shown in Figure 2.13.

![Graphs showing electrical conductivity vs. temperature for in-plane and cross-plane directions.](image)

**Figure 2.13** Electrical Conductivity of SPS sintered Ti$_3$C$_2$T$_x$ Mxene bulk in cross-Plane direction vs. in-plane direction

The Electrical Conductivity versus temperature profile showed that the material is more of semiconducting than metallic in cross-plane direction and more of metallic than semiconducting property in the in-plane direction. Simulations on Mxene materials showed that Mxenes have an intrinsic metallic property and is semiconducting due to the existence functional groups (mainly Oxygen, Fluorine, Hydroxyl)$^{59}$. While the Mxene flakes are sintered into a disk, the joint points between Mxene flakes delivered a good contact between them and the large compressing pressure leads to a macroscale multilayer structure. This could result in an appeared metallic property of the disk in the in-plane direction.
Perpendicular with the orientations of the compressed Mxene flakes, in the cross-plane direction there are gaps between Mxene layers and introduced elements from functional groups. Our intention on electrical conductivity measurement was to invest Lorenz number and further analyze the contributions of thermal conductivity. The anisotropy in these properties would be investigated in the future.

2.4.6 Seebeck Coefficient and special thermal properties of Ti$_3$C$_2$T$_x$ Mxene

Seebeck Coefficients of in-plane and cross-plane sintered Ti$_3$C$_2$T$_x$ Mxene samples were also measured during the property investigation process. The low Seebeck numbers were a great indication of the strong metallic property of Ti$_3$C$_2$T$_x$ Mxene. Seebeck coefficients over the temperature range from near RT to ~430 is shown in Figure 2.14.

![Figure 2.14](image)

Figure 2.14 Seebeck Coefficients of SPS sintered Ti$_3$C$_2$T$_x$ Mxene bulk in cross-plane direction vs. in-plane direction over temperature range from ~40°C to ~ 430°C

Through the experimental results of Seebeck Coefficients over the temperature range electrical contribution of thermal conductivity can be calculated step by step from the following empirical formulas$^{60}$.

$$L = 1.5 + \exp\left(-\frac{|S|}{116}\right) \quad (2.4.9)$$
\[ \kappa_E = L\sigma T \quad (2.4.10) \]

Equation 2.4.9 is an efficient calculation method to obtain the Lorenz number based on single parabolic band model and Equation 2.4.10 is the Wiedemann-Franz Law. By applying these equation, the electronic contribution of thermal conductivity \( K_E \) can be calculated.

![Figure 2.15 Electronic contribution Thermal Conductivity (\( K_E \)) of SPS sintered \( \text{Ti}_3\text{C}_2\text{T}_x \) Mxene bulk in cross-plane direction vs. in-plane direction over temperature range from \( ~40^\circ\text{C} \) to \( ~430^\circ\text{C} \)](image)

Comparing with measured thermal conductivity values of the two samples, theoretical calculated values of \( K_E \) are quite close to the experimental values of thermal conductivity at high temperature range for the in-plane sample. \( K_E \) also contributes a large fraction of thermal conductivity for the cross-plane sample.
CHAPTER 3
FUTURE WORK

3.1 Future work and future expectations of Mxene applications

This novel material, Mxene, has brought great interests in many research fields in the past few years. Applications of Mxenes are not only limited to energy storage and optical devices. There are enormous simulations targeting the potential applications of this material. However, due to the highly hazardous synthesis process and the challenges in surface termination control, many of the simulation results were not verified by experimental methods.

For instance, Zr$_2$C and Hf$_2$C Mxenes as very attractive fresh concepts have brought attentions due to the predicted superior properties in thermoelectric applications and thermal transport application\textsuperscript{61}. The exceptional power factors calculated based on simulations showed that oxygen functionalized Hf$_2$C Mxene could potentially be one competitive nanomaterial in the future thermoelectric field.

Another interesting research direction that was shown in this thesis was the curled structures produced from few layer or single layer mxenes\textsuperscript{62}. Unlike other nanotube structure that have been produced, Mxenes have the features like good flexibility and feasible surface modifications. In other words, it is possible to produce Mxene nanotubes with designated sizes and physical properties. These properties are superior in the field of nanomaterial research. First principle simulations showed that M$_2$CO$_2$ Mxenes have superior thermal conductivities at room temperature and low thermal expansion coefficients\textsuperscript{63}. Carrier mobilities of these materials especially Hf$_2$CO$_2$ is high\textsuperscript{64}. 

Lithium Ion Batteries (FIB) is the field where Mxene materials have been reported the most for industrial applications\textsuperscript{65-67}. The large surface area and definable surface termination has been the greatest advantages of this novel material. Comparing with three-dimensional structure materials like perovskites the layered Mxenes have a much less volume change while functioning as the electrodes material. Which is a good solution for safety problems caused by solid electrolyte interface. The redox active sites could potentially hold more ions comparing with traditional lithium ion battery and make the charge and discharge cycles much more effective.

Along with the advantages, challenges of developing this group of material is also intensive. The main difficulties to overcome from my experimental experience are development of effective synthesis process, synthesis of large lateral size high quality thin flakes, consistency in layer thicknesses and more effective characterizations.

3.2 Insights on future research directions

During the first stage of our project we targeted Hf Mxenes and had many trials on synthesis of Hf\textsubscript{2}CT\textsubscript{x}. At a high temperature of 1900°C, the pulse heating process did not deliver the MAX phase that we expected. The high stability of these metals was a huge difficulty in effective synthesis of these materials. To overcome this barrier, some research groups have utilized Chemical Vapor Deposition (CVD) method for synthesis of two-dimensional transition metal carbides and successfully developed the synthesis method of wall shaped Tungsten Carbide. There are also groups who utilized the relatively more active metal hydrides to lower the synthesis temperature of the MAX phase. The etching agent was also substituted with Lithium Fluoride in Hydrochloric Acid to reduce the hazards involved
in the etching process. From our perspective we utilized the pulsed dc current to activate the precursors to get MAX synthesized with native anisotropy. Although there were reports claimed that the Sparkling Plasma Sintering had no plasma in the sintering process⁶⁸, the anisotropy resulted by the sintering process is undeniable and the relative stronger in-plane direction electrical properties could not be resulted from the pressure which was applied on the cross-plane direction. Yet there is no doubt that the synthesis method introduced Ti-C phases as an impurity which was not eliminated in the following treating process. Also, the synthesis method did not pledge a good homogeneity of the reacting precursors. These were the main reasons that the lattice grains were relatively small. That way the obtained final products’ lateral sizes were not ideal for experimental purposes. More innovative synthesis methods would need to be applied on the synthesis of MAX to obtain large lateral size Mxenes in a large scale. More reliable powder mixing techniques, enhanced chemical vapor deposition synthesis method and liquid assisted grinding process in between etching reactions could all be the new shining points of MAX/Mxene researches in future. It is also crucial to determine the synthesis method’s suitability on the targeted Mxene material.

Transition metal carbides we have researched in this project all had different properties and some of them were not successfully synthesized from our experimental set up. A good example would be the effectively synthesis of Tungsten Carbide from the CVD method, which its synthesis was not reported by any one from any other method.

Another research perspective I would like to bring out is that the intrinsic properties of the novel material is barely studies. Enormous calculations of intrinsic electrical and thermal properties were done yet experimental reports with good correspondence were rare. Many were only an improvement in properties⁶⁹. Energy storage is a great research direction
for Mxene materials. However, not all great natures of Mxenes were utilized in the application. As a hexagonal lattice two-dimensional material with tunable metallic property its intrinsic properties are as important as its thin layers morphology. Characterizations on Mxene materials are still somewhat limited. The synthesis process of Mxenes start all the way from mixing of MAX precursor powders and there were not many reports on the characterizations in between the control process. An ideal analysis on the grain size distribution of synthesized MAX sample could be potentially helpful for further understanding of the material. More precise analysis on the surface terminal group distributions would also be useful for future investigations. By understanding the material better, true potential of it will be present and Mxenes will be serviceable in more significant applications.
REFERENCE


