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Chem. Mater., Just Accepted Manuscript • DOI: 10.1021/acs.chemmater.7b02056 • Publication Date (Web): 05 Jul 2017

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Thermoelectric Properties of Two-Dimensional Molybdenum-based MXenes

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KEYWORDS: MXene, transition metal carbide, thermoelectric, two-dimensional, electrical conductivity.

ABSTRACT: MXenes are an interesting class of 2D materials consisting of transition metal carbides and nitrides, which are currently a subject of extensive studies. Although there have been theoretical calculations estimating the thermoelectric properties of MXenes, no experimental measurements have been reported so far. In this report, three compositions of Mo-based MXenes (Mo2CTx, Mo2TiC2Tx, and Mo2TiC3Tx) have been synthesized and processed into free-standing binder-free papers by vacuum-assisted filtration, and their electrical and thermoelectric properties are measured. Upon heating to 800 K, these MXene papers exhibit high conductivity and n-type Seebeck coefficient. The thermoelectric power reaches 3.09×10² W m⁻¹ K⁻¹ at 803 K for the Mo2TiC2Tx MXene. While the thermoelectric properties of MXenes do not reach that of the best materials, they exceed their parent ternary and quaternary layered carbides. Mo2TiC2Tx shows the highest electrical conductivity in combination with the largest Seebeck coefficient of the three 2D materials studied.

INTRODUCTION

A large class of two-dimensional (2D) transition metal carbides and nitrides, also known as MXenes, has been under extensive investigation since its first discovery in 2011. These atomically thin materials, with general formula of M[n+1]XnT, are usually obtained by selective removal of the “A-element” (Al, Ga, etc.) layers from their ternary layered M[n+1]AXn phase and similar layered precursors. In MXenes, M is an early transition metal, X is carbon and/or nitrogen, T represents the surface functional groups such as OH, O, and/or F groups, and n = 1, 2, or 3. Twenty different MXenes⁴–⁵ have been experimentally synthesized for applications ranging from energy storage,⁴⁻¹⁰ to electromagnetic interference shielding,¹¹ biosensing,¹²⁻¹⁴ ion sieving,¹⁵ water purification,¹⁶ and antibacterial activity.¹⁷ As there are more than 70 different MAX phases that have been experimentally prepared, many more MXenes are expected to be explored.¹⁸

Theoretical studies have predicted that most MXenes are metallic, but few of them (Sc₂CT₅, Ti₂CT₂₆, Zr₂CT₅, and Hf₂CT₇) are predicted to have a non-zero band gap when terminated with appropriate surface groups.¹⁹⁻²¹ These semiconducting MXenes are expected to have a high Seebeck coefficient at low temperatures; e.g., ~1140 µV K⁻¹ and ~2200 µV K⁻¹ at 100 K predicted for Ti₃C₂O and Sc₂C(OH)₂, respectively. According to a later calculation study, Mo₂CF₃ (with fluorine-terminated surface) has been reported to have superior thermoelectric power factor among the other 35 different functionalized M₂XT₅ MXene systems.²² However, those theoretical studies have assumed a fully controlled surface termination, which may be challenging to achieve in experimental studies, where multiple functional groups co-exist. Hope et al reported that the portion of the surface termination groups of Ti₃C₂Tx MXene is dependent on the synthesis routes, and experimentally quantified by ¹H and ¹⁹F nuclear magnetic resonance spectroscopy,²³ where HF etching route results in higher proportion of fluorine termination.

In this work, we report the thermoelectric properties of three kinds of Mo-based MXenes - Mo₂CT₅, Mo₂C₂T₆, and Mo₂C₃T₇. Freestanding MXene papers were fabricated by vacuum-assisted filtration of suspensions of delaminated 2D Mo₂CT₅, Mo₂TiC₂T₆, and Mo₂TiC₃T₇. The latter two compositions were selected instead of Mo₂C₂T₆ and Mo₂C₃T₇, which are not thermodynamically stable and thus difficult to synthesize.²⁴⁻²⁵ Mo₂TiC₂T₆ and Mo₂TiC₃T₇ belong to the family of ordered double-transition-metal carbide MXenes,²⁶ in which Mo atoms are preferentially located in the outer layers, sandwiching the layers of Ti. As a result, all three Mo-based MXenes that we synthesized in this study have Mo atoms on the surface, creating a similar surface chemistry. Additionally, these Mo-based MXenes with oxygen termination have been reported as 2D topological insulators, based on calculation along with the consideration of spin-orbit coupling.²⁷⁻²⁸ 2D topological insulators with controlled size have been predicted to show anomalous Seebeck effects,²⁹ and the best thermoelectric material, Bi₂Te₃, and its alloys are also topological insulators.³⁰ This provided additional motivation for studying transport properties of these MXenes.
Experimental Methods

Synthesis of MXene freestanding papers. To synthesize Mo$_2$CT$_x$, Mo$_2$TiC$_2$T$_x$, and Mo$_2$Ti$_3$C$_2$T$_x$ MXenes, 2g of Mo$_2$Ga$_2$C powder was slowly added into 80 ml of 25% aqueous hydrofluoric acid (HF), and for Mo$_2$TiAlC$_2$ and Mo$_2$Ti$_3$AlC$_2$ MAX phases 20 ml of 50% HF were used. The precursor carbides were slowly added into the acidic solutions which were cooled by ice-bath to minimize the localized heating. The mixtures were then stirred with a magnetic Teflon stir bar at 55°C for 160 h, 48 h, and 96 h, respectively. After etching, the mixtures were washed several times until the pH reached around 6. For each washing step, 40 ml of deionized (DI) water was added into centrifuge tubes, hand shaken for 1 min, centrifuged at 5000 rpm for 2 min, and then discarded the supernatant. The solid sediments were kept in a vacuum oven at RT overnight for drying. 1g of dried multilayer MXene powder was further re-dispersed into 80 ml of 10% tetrabutylammonium hydroxide (TBAOH) solution for intercalation, and stirred for 4 h (Mo$_2$CT$_x$, Mo$_2$TiC$_2$T$_x$) or 18 h (Mo$_2$Ti$_3$C$_2$T$_x$) at RT. The resulting mixtures were washed two times, and sediments were re-dispersed into DI water followed by ultra-sonication for an hour. The mixtures were later centrifuged at 5000 rpm for 1 hour, and the resulting supernatants were carefully collected. The suspension solutions were vacuum filtrated through a porous membrane (3501, surfactant-coated PP, Celgard, USA), and the vacuum filtrated papers were carefully peeled off for the experiment. 50% HF and 54-56% TBAOH were purchased from Aldrich.

Thermoelectric properties measurement. Electrical conductivity and Seebeck coefficient of MXene paper were measured in the in-plane direction under dynamic flow of Ar/H$_2$ reducing ambient. The measurements were done in the temperature range of 300-800 K, using a commercially available thermoelectric tester RZ2001i (Ozawa Science Co. Ltd., Japan). At each temperature, electrical conductivity were measured under thermal equilibrium by 4-point linear probe method. After that, a small thermal gradient was generated by local cooling of one side of sample (local cooling was done by air circulation through one of the quartz sample holder pipe). Among the four linear probes, two of the inner probes are thermocouple-probes, so the temperature difference (ΔT) and the voltage difference (ΔV) can be measured across the sample. Five different data points were collected at each temperature, and the Seebeck coefficient could be calculated by finding the linear fit slope (ΔV/ΔT). As the measured Seebeck coefficient is the difference between the sample and the platinum electrode (S$_{measured}$ = S$_{sample}$ – S$_{electrode}$), corresponding Seebeck coefficient of Pt at the temperature was accounted for to find the Seebeck coefficient of the sample. Thermal history for the measurement is shown in Figure S6. Further details on the measurement can be found elsewhere.

Characterization. X-ray diffraction (XRD) patterns were collected by a Bruker diffractometer (D8 advance, AXS system, Germany) with Cu Kα radiation, λ = 1.5406 Å. For the precursor carbides, small amounts of powder were loaded into a small cavity of the sample holder and pressed using a glass slide. For MXene, a single slice of MXene paper was placed on a zero-diffraction plate. Cross-section morphologies were observed by FE-SEM (Nova Nano 630, FEI, USA). The Raman spectra were collected by a micro-Raman spectrometer (LabRAM Aramis, Horiba, Japan) equipped with a long working distance x50 objective lens (LMPLFLN50X, Olympus, Japan) using 473 nm excitation (04-01 series, Cobalt blues™, Sweden) at RT. Thermal analysis (TGA-DSC) was carried out by STA 449 F1 Jupiter (Netzsch, Germany) with the heating rate of 5 K min$^{-1}$ under Ar ambient, using Al$_2$O$_3$ crucibles. Carrier concentration and Hall mobility were measured by a Hall-effect measurement system (Lake Shore 7700A) using van der Pauw technique at RT under a magnetic field range of ± 5, 10, 15, and 20 kG. Ohmic contact was achieved by using fast drying silver paste.

RESULT AND DISCUSSION

Figure 1 shows a schematic illustration of the MXene synthesis process. The ternary and quaternary carbide precursor powders (Mo$_2$Ga$_2$C, Mo$_2$TiAlC$_2$, and Mo$_2$Ti$_3$AlC$_2$) were first chemically etched by hydrofluoric acid (HF) which attacks the metallic M-A bond. After washing in deionized water several times, these multilayer MXenes (HF-etched powders) were further reacted with tetrabutylammonium hydroxide (TBAOH) which leads to exfoliation of 2D MXene suspensions by intercalation of tetrabutylammonium cation (TBA$^+$) between the negatively charged MXene sheets, followed by further washing and sonication. Details of the synthesis process are explained in the experimental section. Scanning electron microscopy (SEM) images of the precursors and multilayer MXenes (Figure S1) show the typical layered
structure of the ternary and quaternary carbides and separations between layers after chemical etching in the multilayer MXenes.

Figure 2(a) shows a digital photograph of Mo$_2$CT$_x$, Mo$_2$TiC$_2$T$_x$, and Mo$_2$Ti$_2$C$_3$T$_x$ freestanding papers, which were peeled off from a porous membrane after vacuum-assisted filtration and cut into 1×1 cm$^2$ squares for thermoelectric property measurements. Those freestanding paper samples are usually flexible in the pristine state without the use of binder additives, as shown in Figure 2(b). The flexibility can be altered upon annealing unless the nanosheets are supported by a flexible substrate. To achieve both high electrical conductivity and flexibility of MXene paper in pristine or mild dried state, cation intercalation can be used instead of organic intercalation as demonstrated in Ti$_2$C$_3$T$_x$ MXene.  

Figure 2(c-h) show cross-sectional SEM micrographs of the as-synthesized Mo-based MXene papers (pristine) and after the thermoelectric measurements from room temperature (RT) to 800 K (annealed). The typical layered structure due to the restacking of MXene flakes is clearly observed in the pristine MXene papers. The cross-sectional SEM images of the annealed MXene papers show more compact structures, which lead to increased electrical conductivity, as will be discussed later.

X-ray diffraction (XRD) patterns of the parent layered carbides with corresponding MXene papers in pristine and annealed states are presented in Figure 3(a-c). Pristine MXene papers (middle patterns) show a large shift of the (002) peak toward lower angles compared to corresponding parent carbide precursor phases (bottom patterns). This result suggests an increase in the c-lattice parameter (c-LP) in the MXene papers due to the surface functional groups replacing the ‘A’ element layers, as well as the presence of intercalated TBA$^-$ and water molecules between the MXene nanosheets. After annealing the MXene papers at 800 K (top patterns), the (002) peak shifts back to higher angles, which can be explained by a decrease in the c-LP due to the removal of the intercalated molecules, OH and some other terminations. For Mo$_2$Ga$_x$C and its MXene (pristine and annealed, Figure 3(a)), the (002) peaks are centered at 9.76°, 5.24°, and 11.17°, respectively. The corresponding c-LPs are 18.1 Å, 33.7 Å, and 15.8 Å. The interlayer spacing between Mo$_2$C layers in pristine Mo$_2$CT$_x$ compared to Mo$_2$Ga$_x$C increased by ~7.8 Å. In Mo$_2$Ga$_x$C, two atomic layers of Ga separate the Mo$_2$C layers. After etching and delamination, these Ga layers are replaced by surface terminations and intercalated TBA$^-$ and water molecules. After annealing the Mo$_2$CT$_x$ paper, the interlayer spacing decreased by ~8.9 Å, due to the removal of intercalated molecules and cations. Mo$_2$CT$_x$ with no intercalated molecules has been calculated to have similar c-LP. Considering the synthesis process described above, one observes a large change in the interlayer distance, which is due to the intercalation (pristine MXene) and removal of organic molecules (annealed MXene).

A similar trend can be found in Mo$_2$TiAlC$_2$ (Figure 3(b)), where the c-LP value first increases from 18.5 Å for the precursor (Mo$_2$TiAlC$_2$) to 37.8 Å after etching the Al layers and intercalation, and decreases to 24.5 Å due to the removal of intercalated organic and water molecules during heating to 800 K. In the case of Mo$_2$Ti$_2$AlC$_3$ (Figure 3(c)), the initial c-LP value is 23.4 Å based on the (004) peak position at 15.1° for the Mo$_2$Ti$_2$AlC$_3$, and it increases to 42.6 Å for the pristine Mo$_2$Ti$_2$C$_3$T$_x$ paper and decreases to 27.6 Å after annealing. The crystallographic ionic diameter of TBA$^-$ is known to be around 9.9 Å, however a minor distortion/conformation of butyl chains allows the intercalation into 8 Å interlayer space. Thus, the observed shifts for the basal plane related peak positions correlate with the intercalation and de-intercalation of TBA$^-$ and water molecules.

Figure 3(d-f) shows the Raman spectra of three Mo-based layered carbide precursors (bottom) and their corresponding pristine (middle) and annealed MXenes (top). There are clear changes in the Raman spectra after etching that show disappearance and/or shift of the Raman active vibration modes...
Figure 3. (a-c) X-ray diffraction patterns and (d-f) Raman spectra of the parent layered carbide phases and corresponding pristine and annealed MXene papers. (a,d) Mo$_2$Ga$_x$C and Mo$_2$CT$_x$, (b,e) Mo$_2$TiAlC$_x$ and Mo$_2$TiC$_x$T$_x$, (c,f) Mo$_2$Ti$_3$AlC$_3$ and Mo$_2$Ti$_3$C$_3$T$_x$. There are no XRD peaks below 8 degree in patterns of precursors. There are no Raman peaks above 800 cm$^{-1}$ in the spectra of precursors.

Figure 4(a-c). All three MXene papers are highly resistive in the pristine state near RT, but their electrical conductivity increases rapidly during the first heating cycle, with three identifiable regimes: (1) Removal of water molecules gradually enhances the conductivity at low temperatures (300-500 K). (2) Thermal decomposition of TBA$^+$ intercalant at around 500-600 K. The onset of rapid conductivity increase is well matched to the reported thermal decomposition temperature of TBA$^+$ intercalant in graphite, which is around 480 K.$^{36}$ (3) Above 600 K, the conductivity increases slowly which can be ascribed to the decomposition of remaining TBA$^+$ and the possible thermal elimination of surface termination groups. It should be noted that the observed temperature dependent electrical conductivity during the 1$^{st}$ heating cycle is the sum of both irreversible changes due to thermal de-intercalation, and reversible thermal response of the material itself, where the former factor is more dominant. The MXene flakes are likely to undergo re-arrangement throughout the thermal heating process described above, where the interlayer spacing decreases. In order to confirm the above hypothesis about the cause of the conductivity change during the first heating cycle in MXenes, thermal gravimetric analysis (TGA) was carried out along with differential scanning calorimetry (DSC) for Mo$_2$Ti$_3$C$_3$T$_x$ paper, as shown in Figure 4(d). An overall weight loss of around 8% was observed from RT to 800 K under Ar ambient. The quantity of intercalated water molecules in pristine Mo$_2$Ti$_3$C$_3$T$_x$ is estimated around 1.6 wt% based on the weight loss below 500 K.$^{42}$ Most of weight loss (5.3 wt%) between 500-650 K can be attributed to the thermal de-intercalation of TBA$^+$, and this temperature range matches the one in which electrical conductivity of MXenes shows a significant increase. This result suggests that the MXene flakes in the pristine paper are separated by large intercalant molecules, but come in closer contact that enhances the carrier transport due to the thermal de-intercalation process at around 500-600 K. These changes, also supported by XRD studies (Figure 3(a-c)), are irreversible and are not observed in the 2$^{nd}$ thermal cycle of TGADSC, nor during the 2$^{nd}$ thermal cycle of thermoelectric properties measurement (Figures S3-S5). At above 650 K, only ~1 wt% of weight loss was observed, while the electrical conductivity slowly increased. Despite the small changes in both weight and electrical conductivity above 650 K, relatively...
Figure 4. (a-c) Temperature dependent thermoelectric properties of Mo-based MXene papers during the first thermal cycle. (a) Electrical conductivity, (b) Seebeck coefficient, and (c) thermoelectric power factor. The heating cycle and subsequent cooling cycle are marked by filled symbols and open symbols, respectively. The blue triangle, green circle, orange diamond symbols represent Mo$_2$CT$_x$, Mo$_2$TiC$_2$T$_x$, and Mo$_2$Ti$_2$C$_3$T$_x$, respectively. (d) TGA curve (green) with first derivative of weight (black) and DSC curve (red) of Mo$_2$TiC$_2$T$_x$ for the first heating cycle.

A large endothermic heat flow was observed during both the first and second thermal cycle. Considering that the weight change in second thermal cycle is nearly zero (Figure S4(d)), the heat could be absorbed due to the removal of surface functional groups, as earlier observation for Ti$_3$C$_2$T$_x$. Since the surface functional groups are known to accept electrons from MXenes, removal of surface terminations can be another contributor to the increase in electrical conductivity.

The electrical conductivity of pristine Mo$_2$CT, measured before annealing is 0.8 S cm$^{-1}$, but increases to 1252 S cm$^{-1}$ at the end of the first thermal cycle (heating and then cooling to near RT) during thermoelectric measurements. This result is in agreement with literature, where the RT electrical conductivity of Mo$_2$CT was shown to increase by two orders of magnitude after drying at 120°C for 18 hours under vacuum. The conductivity values of pristine (annealed) Mo$_2$TiC$_2$T$_x$ and Mo$_2$Ti$_2$C$_3$T$_x$ are 44 S cm$^{-1}$ (1494 S cm$^{-1}$) and 15 S cm$^{-1}$ (614 S cm$^{-1}$), respectively. Table 1 shows a summary of the Hall-effect measurement results. Pristine Mo-based MXene papers typically have carrier density of $\sim$10$^{20}$ cm$^{-3}$ with a Hall mobility of 10$^{-2} \sim 10^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$. Annealed Mo-based MXene papers exhibit one order of magnitude higher carrier concentration with Hall mobility of few cm$^2$ V$^{-1}$ s$^{-1}$. The changes in conductivity during the first annealing are attributed to the decreased interlayer spacing due to thermal de-intercalation and partial de-functionalization of MXenes. Once the conductivity stabilizes after the first heating cycle, Mo$_2$CT$_x$ and Mo$_2$TiC$_2$T$_x$ exhibit metallic behavior while Mo$_2$Ti$_2$C$_3$T$_x$ shows semiconductor-like behavior, based on the slope of temperature dependence of conductivity in the stabilized (annealed) state. These characteristics are related to the carrier concentration and may have also been affected by the stacking structure, where annealed Mo$_2$CT$_x$ and Mo$_2$TiC$_2$T$_x$ exhibit well aligned nanosheets (Figure 2(d,f)), while annealed Mo$_2$Ti$_2$C$_3$T$_x$ films look less compacted (Figure 2(h)). Larger thickness of Mo$_2$Ti$_2$C$_3$T$_x$ nanosheets could make their rearrangement and film densification more difficult, but we did not find a good way to quantify those differences.
The Seebeck coefficient of these MXenes were simultaneously measured as shown in Figure 4(b). All three MXenes show n-type behavior, as indicated by the negative values of the Seebeck coefficient. Unlike the rapid change in electrical conductivity, the Seebeck coefficient does not show a drastic transition; instead it undergoes a slow change during the first heating cycle. This observation is another evidence that supports the fact that the rapid increase in the electrical conductivity above ~500 K (Figure 4(a)) is likely due to the enhanced electrical network between MXene nanosheets rather than irreversible changes of each MXene flakes. As the nanosheets get better connection during the first heating cycle, the energy barrier between MXene flakes will spontaneously decrease, hence a larger numbers of domains will contribute to its overall Seebeck coefficient. Particularly, Mo₂CT₃ samples shows an interesting transition from p-type to n-type upon thermal annealing, as confirmed by both Hall-effect measurement and thermoelectric test. The spontaneous transition of its Seebeck coefficient seems to be a result of a decreased energy barrier at the edges of MXene flakes during the first heating cycle.

Just like electrical conductivity, the Seebeck coefficient of all three MXenes reaches a steady-state value and remains stable after the first heating cycle, as shown in Figures S3-S5. The temperature dependent Seebeck coefficient is quite linear with temperature, indicating absence of any magnetic transition. Mo₂Ti₃C₅Tₓ exhibits the smallest Seebeck coefficient, among the three samples, of ~27.5 μV K⁻¹ at 803 K, while Mo₂CT₃ exhibits ~30.5 μV K⁻¹ at 798 K. These two compositions have similar temperature dependent Seebeck coefficient. Mo₂CF₂ has been theoretically predicted to be semiconducting with a large Seebeck coefficient (> 100 μV K⁻¹ at 400 K) and a negative correlation between Seebeck coefficient and temperature. However, our experimental results show the opposite. This suggests that the prepared Mo₂CT₃ may not be dominated by fluorine termination, despite the fact that we used an HF etching method. It has been reported that delamination of Mo-containing MXenes with TBAOH reduces the fluorine content. In contrast, Mo₂Ti₃C₅Tₓ exhibited a larger Seebeck coefficient of ~47.3 μV K⁻¹ at 803 K, along with the largest slope. It is worth to note that the observed Seebeck coefficient of Mo₂Ti₃C₅Tₓ MXene paper is higher than the theoretically calculated value of its parent Mo₂TiAlC₂ MAX phase.

Due to its high conductivity (1380 S cm⁻¹ at 803 K) and large Seebeck coefficient (~47.3 μV K⁻¹ at 803K), Mo₂Ti₃C₅Tₓ shows the largest thermoelectric power factor of 3.09 × 10⁻⁴ W m⁻¹ K⁻² at 803 K among the MXenes studied here, as shown in Figure 4(c). Mo₂TiC₅Tₓ also shows nearly one order of magnitude higher power factor near RT compared to chemically exfoliated WS₂, which has been demonstrated as a wearable thermoelectric generator. This superior thermoelectric power factor of Mo₂TiC₅Tₓ can be attributed to its electronic band structure. One possible explanation is the so-called “pudding-mold” type band structure found in high performance thermoelectric materials such as Na₂CoO₃ and CuAlO₂. The band near the Fermi level can be flatter depending on the ratio of hopping integrals to the first, second, and third nearest neighbor sites on the triangular lattice, where the peculiar shape band structure can result multiple Fermi surfaces that can contribute to the conductivity overcoming the decrease in Seebeck coefficient. Such variable range hopping behavior can be related to the geometrical frustration in triangular lattice with the antiferromagnetic spin interaction. However, more theoretical work is needed to confirm this hypothesis. According to the simulation studies on the electronic band structure of Mo₂-based MXenes with oxygen termination, Mo₂TiC₅O₂ certainly shows a much larger portion of flat band near the Fermi level than Mo₂CO₂ and Mo₂Ti₃C₅O₂, which can be the origin of coexistence of metallic conductivity and a relatively larger Seebeck coefficient. Due to the highly conductive nature of MXenes, hybrid materials with outstanding thermoelectric performance may be produced by combining MXenes with large band gap semiconductors to increase the overall Seebeck coefficient and/or polymers to decrease the thermal conductivity.

**Conclusion**

In summary, we have reported the first experimental measurements of the temperature dependent thermoelectric properties of Mo₂-based MXenes up to 800 K. A combination of a high electrical conductivity (1380 S cm⁻¹ at 803 K) and a relatively large Seebeck coefficient (~47.3 μV K⁻¹ at 803K) has been found for Mo₂TiC₅Tₓ, with its thermoelectric power factor reaching 3.09 × 10⁻⁴ W m⁻¹ K⁻² at 803 K. The conductivity of all MXenes studied in this work shows a rapid increase above ~500 K, which is due to de-intercalation of water and organic molecules, as well as partial loss of functional groups resulting in a decrease of interlayer spacing and improved contacts between the MXene nanosheets. Raman spectroscopy analysis revealed that Mo₂-based MXenes are thermally robust upon annealing at up to 800 K under Ar/H₂ ambient. Further enhancement in thermoelectric performance of MXenes can be achieved by additional doping, controlling the surface functional groups, and/or hybridization with semiconductor materials or polymers.

**ASSOCIATED CONTENT**

Supporting Information. SEM images of precursor materials and HF-etched multilayer MXenes; Extended Raman spectra of annealed MXene papers; Thermoelectric data for 2nd thermal cycle; Raman spectroscopy analysis of Mo₂-based MXenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions
All authors have given approval to the final version of the manuscript.

Funding Sources
Support for research reported in this publication was provided by King Abdullah University of Science and Technology (KAUST).

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENT
The authors thank Dr. Narendra Kurra for useful discussions and Dr. Rajeshkumar Mohanraman for technical help in TGA-DSC analysis.

REFERENCES


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