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Metallic MXenes: A new family of materials for flexible triboelectric nanogenerators

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Abstract (200 words): Wearable and flexible electronics warrant the development of self-powered devices to circumvent the limitations imposed by traditional energy storage devices. Triboelectric nanogenerators (TENGs) that convert waste mechanical energy from human motions into electric power offer a solution. Highly electronegative and yet conducting TENG materials that support the generation of *both* large potential differences and high currents are imperative for effectively harvesting electric power from human muscle movements. Here, we demonstrate that two-dimensional titanium carbide MXenes ($\text{Ti}_3\text{C}_2\text{T}_x$, where T_x stands for surface functional groups such as -O, -OH, and -F) are a new family of electrically conducting materials that are triboelectrically more negative than polytetrafluorethylene or Teflon. Specifically, flexible MXene TENGs support both high open circuit voltages ranging from ~500 to ~650 V and an instantaneous peak power up to ~0.5 – 0.65 mW that could power >60 light-emitting diodes or quickly charge a 1 μF capacitor up to 50 V. Lastly, we

demonstrate that flexible MXene TENGs are capable of harvesting electrical power from simple muscle movements (e.g., texting) even when the device is flexed by $\sim 30^\circ$ suggesting facile integration with wearable electronics.

The advent of portable and handheld electronics is imposing a greater demand on the global energy resources. Electronic devices, such as mobile phones and laptops, account for a large portion of the global electricity consumption [1]. Flexible electronics aims to transform portable devices powered by batteries into low-power (mW- μ W) wearable devices that can be integrated into everyday clothing [2–7]. In this regard, a promising approach is to harvest the energy dissipated in the movements of the wearer using triboelectric nanogenerators (TENGs) to develop self-powered wearable devices [8–17]. A TENG harvests waste mechanical energy by bringing two electrodes into contact in different configurations such as: i) the vertical contact separation mode [18,19], ii) the in-plane sliding mode [20–24], iii) the single-electrode mode [25–28], and iv) the free standing triboelectric layer mode [29,30]. In a TENG, charge transfer occurs between electrodes during intermittent contact according to the differences in their electronegativity. This generates an electrical potential difference (V) between the oppositely charged electrodes ($\pm Q$) separated from each other, much like a capacitor, and the energy $E=QV/2$ could be harvested in the form of electrical energy using an external circuit. The overall performance of a TENG depends on the contact-induced voltage across the electrodes and the maximum current (dictated by the electrical conductivity of TENG electrodes) that could be drawn from the device [31]. The electrical potential difference in a TENG can be maximized by a judicious choice of electrode materials in the triboelectric series [32] (materials ranking based on their charge affinity measured in Coulomb/Joule). However, the electrode materials must also be electrically conducting for harnessing useful electrical power from a TENG. While electrical conductors that are triboelectrically positive and ranked high in the triboelectric series do exist (e.g., Al, see

supporting information Fig. S1), electrical conductors that are triboelectrically negative are lacking.

One of the highly ranked triboelectrically negative materials is polytetrafluorethylene or PTFE [32], which has been widely used in TENGs for achieving large potential differences. Although many unique features of PTFE such as its low friction coefficient, low dielectric constant, good mechanical strength and excellent plasticity are attractive for TENG applications [33], PTFE-based TENGs are often limited to single-electrode mode operation due to the electrically insulating nature of PTFE. The high chemical and thermal stability of PTFE along with its low surface energy (~ 18 mN/m) [35] precludes facile fabrication of electrically conducting PTFE composites or the deposition of metallic coatings on PTFE. Similar challenges exist for other electronegative polymer materials such as polydimethylsiloxane (PDMS) and fluorinated ethylene propylene (FEP). These limiting factors of electronegative polymers (e.g., PTFE, PDMS, and FEP) seriously impede the realization of TENGs that can produce both large potential differences and currents.

Here, we overcome these limitations using an emerging family of two-dimensional layered transition metal carbides and/or nitrides, known as MXenes [36–38], that have recently been demonstrated for many applications including energy storage [36], EMI shielding [39], and gas sensors [40]. MXenes, a family of ~ 30 synthesized material compositions and millions predicted theoretically [41], offer a wide range of electrical and mechanical properties that can be tuned by altering the composition and the surface terminations [36,37]. The general formula for MXenes is $M_{n+1}X_nT_x$ ($n=1-3$), where M stands for a transition metal (e.g., Ti, Sc, Cr, Mo, Zr, Hf, Nb, Ta, etc.), X stands for carbon or nitrogen, and T_x stands for surface terminations, such as =O, -OH, and -F (Figure 1a). We demonstrate that $Ti_3C_2T_x$ MXene can be used as an ideal electrically conducting (~ 6000 - 10000 S/cm) [42,43] TENG electrode which has a highly electronegative surface due to -F, as well as oxygen containing terminating functional groups. Specifically, we show that $Ti_3C_2T_x$

MXene is on par with PTFE in the triboelectric series, and thus provides a much-needed solution to surmount the inherent conductivity limitations of electronegative polymers (PTFE, PDMS, and FEP). MXene TENGs ($2.5 \times 5 \text{ cm}^2$) generated potential differences as high as $\sim 650 \text{ V}$ with a maximum peak power of $\sim 0.65 \text{ mW}$. These devices showed good flexibility and long lifetime (50,000 cycles) without a loss of performance for bending angles as high as 30° during energy harvesting from routine typing and texting.

As described in the experimental section, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene powders were synthesized by selective etching of Al atomic layers from Ti_3AlC_2 using LiF-HCl solution [36,39,44]. The $\text{Ti}_3\text{C}_2\text{T}_x$ thin films were fabricated by spray coating an aqueous suspension of $\text{Ti}_3\text{C}_2\text{T}_x$ on glass (referred as MXene/Glass) and ITO coated polyethylene terephthalate (or MXene/PET-ITO). A detailed characterization of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene powders and thin films can be found in previous publications [36,38,45,46]. MXene TENGs ($2.5 \times 5 \text{ cm}^2$) were assembled by separating bottom MXene/Glass or MXene/PET-ITO electrodes from the top PET-ITO electrode using $\sim 1 \text{ mm}$ thick insulating glass pads serving as spacers (Figures 1b-d). $\text{Ti}_3\text{C}_2\text{T}_x$ coatings on the bottom electrode and the PET side of the top electrode form the contacting surfaces in a MXene/Glass:PET-ITO TENG (Figure 1d). To confirm the hypothesis that $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is on par with PTFE in the triboelectric series, a similar TENG ($2.5 \times 5 \text{ cm}^2$) was fabricated with PTFE as the bottom electrode and PET-ITO as the top electrode (referred to as PTFE:PET-ITO).

Figure 1. (a) Structure of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. A MXene triboelectric nanogenerator (MXene TENG) was assembled as shown in schematics (b-d). An aqueous solution of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene coated on glass or PET-ITO films (b) was used as the bottom electrode for MXene TENG while a PET-ITO film was used as the top electrode. The electrodes were separated from each other using ~ 1 mm thick insulating glass spacers (c). (d) A schematic of MXene TENG (with MXene/Glass as the bottom electrode) in its natural state with a 1 mm air gap separating top and bottom electrodes. (e) A home-built impactor with a ~ 1 " diameter mandrel applied a ~ 15 N vertical force to MXene TENG at ~ 2 Hz frequency. Copper (Cu) wires were attached to both top and bottom electrodes for electrical characterization.

The TENGs were tested by subjecting them to a vertical compressive force of ~ 15 N at a frequency of 2 Hz using a custom-built impactor (see Figure 1e and video MXTENG- $\text{Ti}_3\text{C}_2\text{T}_x$ -Glass in the SI section). As shown in Figures 2a and 2b, MXene/PET-ITO:PET-ITO and PTFE:PET-ITO TENGs showed a similar response in single-electrode mode operation (see Figure S2 in the SI section) with open-circuit voltages (V_{oc}) oscillating between -180 and 500 V. The underlying mechanism for converting mechanical energy into potential difference in single-electrode MXene/PET-ITO:PET-ITO TENG is similar to conventional PTFE-based TENGs [18,19,47] and may be described as follows. When the top PET-ITO electrode comes into contact with the bottom MXene/Glass electrode, the surface functional groups (particularly, $-\text{F}$) [48,49] present on MXene lead to a charge transfer between the two electrodes ensuing in the observed V_{oc} . The amount of charge transfer and V_{oc} are dependent

on the difference in the electronegativities of the bottom (MXene/Glass) and top (PET-ITO) electrodes. Thus, replacing one of the electrodes with another material of a different electronegativity (e.g., Kapton or polyimide instead of PET-ITO) changes the amount of charge transfer and V_{oc} (see Figure S3).

Figure 2. The single-electrode mode responses of TENGs. (a) MXene/Glass:PET-ITO TENG when subjected to a 15 N vertical force at 2 Hz yields a large open circuit voltage (V_{oc}) that oscillates between -180 and 500 V at the same frequency as the applied force. (b) PTFE:PET-ITO TENG (with the same applied force as in (a)) yields a similar V_{oc} oscillating between -190 and 500 V. (c) MXene/Glass:PTFE TENG subjected to the same loading regime as in (a) does not yield a V_{oc} suggesting the lack of charge transfer between $Ti_3C_2T_x$ MXene and PTFE due to their similar electronegativities. The schematics of single-electrode mode for (a), (b) and (c) are shown in (d), (e) and (f).

The similar V_{oc} observed for MXene/Glass:PET-ITO and PTFE:PET-ITO in single-electrode mode (*cf.* Figure 2a and 2b) imply that both $Ti_3C_2T_x$ MXene and PTFE are placed equally below PET/ITO on the triboelectric series. This assertion was further confirmed by fabricating a MXene/Glass:PTFE TENG (Figure 2c), which showed no output voltage due to similar electronegativities arising from -F groups in both PTFE and MXene (see inset in Figure 2c). While PTFE:PET-ITO TENGs are limited to single-electrode mode operation due to the insulating nature of PTFE, MXene-based TENGs are advantageous as they can be operated in the two-electrode vertical contact separation mode (Figure S2).

Figure 3. (a) Upon subjecting a MXene/Glass:PET-ITO TENG to a 15 N vertical force at 2 Hz, generated a large V_{oc} that oscillated between -200 (press cycle) and 650 (release cycle) V at the same frequency as the applied force. (b) A magnified view of V_{oc} depicted in panel (a). (c) Flexible MXene/PET-ITO:PET-ITO TENG exhibited a similar performance with V_{oc} oscillating between -180 (press cycle) and 500 V (release cycle). (d) A magnified view of V_{oc} depicted in panel (c). In panels (b) and (d), the extra spike in V_{oc} (highlighted in the dashed green boxes) occurs due to the microscopic bouncing of the top PET-ITO electrode at the end of each pressing cycle.

Initially, MXene TENG in the two-electrode vertical contact separation mode is in a neutral state with no induced charges in the device. When the electrodes in MXene TENG are brought into contact during the pressing cycle, the $Ti_3C_2T_x$ coating readily attracts triboelectrically generated electrons from PET due to electronegative surface groups (T_x) such as =O and -F (similar to PTFE). Although the bottom MXene/Glass electrode (/top PET-ITO electrode) is negatively (/positively) charged at the end of the pressing cycle, no net potential difference develops across the MXene TENG when the electrodes are in contact. Upon

removing the applied force in the following releasing cycle, the top PET-ITO electrode moves away from the bottom MXene/Glass electrode ensuing in charge redistribution and a potential difference between the two electrodes. At the end of the releasing cycle, a significantly high $V_{oc} \sim 650$ V was measured (Figures 3a and 3b). The MXene TENG in this state is comparable to a capacitor with two oppositely charged electrodes (viz., $Ti_3C_2T_x$ and PET) separated by a distance x with $V_{oc} = \sigma x / \epsilon$, where σ is the surface charge density and ϵ is the dielectric constant between the two electrodes. In the subsequent pressing cycle, x decreases as the electrodes are pushed towards each other leading to a decrease in V_{oc} . When the electrodes are again brought into contact at the end of the pressing cycle, charge injection occurs due to the triboelectric effect leading to a $V_{oc} \sim -200$ V. Although both pressing and releasing cycles result in a potential difference between the electrodes, they are not symmetric because they involve different effects viz., contact-induced electrification and charge redistribution, respectively. In the following cycles, V_{oc} oscillates between -200 V (pressing) and 650 V (releasing) with the same frequency (~ 2 Hz in this case) as the applied force on MXene TENG (Figures 3a and 3b). Based on the measured $V_{oc} \sim 650$ V and $V_{oc} = \sigma x / \epsilon$, a maximum surface charge density $\sigma \sim 6.1 \mu C m^{-2}$ is expected for each electrode. As shown in the supporting information Figures S4 and S5, finite-element simulations using COMSOL Multiphysics concur with these experimental observations.

In the experiments described thus far, $Ti_3C_2T_x$ was coated on the bottom glass electrode while the top counter electrode was made of flexible PET-ITO. To fabricate a fully flexible TENG, the bottom glass substrate was replaced with a PET-ITO film and coated $Ti_3C_2T_x$ on the PET side (referred to as MXene/PET-ITO:PET-ITO). The flexible TENG was also tested using a 15 N force at 2 Hz similar to the MXene/Glass:PET-ITO TENG. The flexible TENG generated a slightly lower $V_{oc} \sim -180$ V (pressing) and 500 V (releasing) (Figures 3c and d), which is attributed to warping of the bottom MXene/PET-ITO electrode

due to the absence of a rigid support. In addition to characterizing the flexible TENG in the open circuit configuration with no electrical load, the output voltage and current under varying electrical load conditions were also measured (Figure 4). The V_{oc} increased (red curve in Figures 4a and 4b) with increasing load resistance with a concomitant decrease in current (blue curve), which is in accordance with Ohm's law. A maximum peak power of ~ 0.65 and ~ 0.50 mW was obtained using MXene/Glass and MXene/PET-ITO as the bottom electrodes, respectively (Figures 4c and 4d).

Figure 4. (a, b) Output voltages and currents generated in the pressing cycle for both rigid and flexible MXene TENGs as a function of electrical load resistance. In case of MXene/Glass:PET-ITO (MXene/PET-ITO:PET-ITO) TENG, a maximum V_{oc} of ~ 650 V (500 V) and short circuit current of $\sim 7.5 \mu A$ ($6.3 \mu A$) is produced. (c, d) Output power as a function of varying load resistances for both MXene/Glass:PET-ITO and MXene/PET-ITO:PET-ITO TENGs. A maximum peak power of ~ 0.65 and 0.5 mW are generated for MXene/Glass:PET-ITO and MXene/PET-ITO:PET-ITO, respectively. Although the MXene/PET-ITO:PET-ITO TENG produced slightly less electrical power, it was sufficient to light >60 LEDs, as shown in the inset (d).

To demonstrate the suitability of MXene TENGs in practical applications such as powering electronics that require a fixed voltage, a capacitor ($1\ \mu\text{F}$) was charged by the rectified output of the TENGs described in Figure 4 (see supporting information Figure S6). Because each pressing-and-releasing cycle produces only a small increment in the voltage of the capacitor, the capacitor approximates a constant voltage load (similar to a battery or an electronic device). As shown in Figure S6, the MXene/Glass:PET-ITO (/MXene/PET-ITO:PET-ITO) could charge a $1\ \mu\text{F}$ capacitor to a voltage of $\sim 55\ \text{V}$ ($/40\ \text{V}$) within ~ 8 minutes when subjected to a $15\ \text{N}$ force at $2\ \text{Hz}$. Despite the relatively low output voltage and power of MXene/PET-ITO:PET-ITO TENG, it powered ~ 60 LEDs as shown in the inset in Figure 4d (and video MXTeng-PET-ITO powering LEDs in the SI section).

Figure 5. (a-c) The flexible MXene TENG was clamped at 30° and flexed with a force of $\sim 1\ \text{N}$ applied at $2\ \text{Hz}$ by the mandrel. (d) Flexing MXene TENGs produced a potential difference between -40 and $65\ \text{V}$ despite a significantly smaller force compared to pressing force of $\sim 15\ \text{N}$ used in Figure 4. (e) A magnified view of the voltage profile generated by the flexible MXene TENG.

To further test the performance of flexible MXene/PET-ITO:PET-ITO TENG, it was clamped at one end at an angle of 30° relative to the horizontal (Figures 5a-c), and its free end was subjected to a 1 N force at 2 Hz. As shown in Figures 5d and 5e, robust outputs of $V_{oc} \sim -40$ (pressing) and 65 (releasing) V were obtained, which are smaller compared to V_{oc} obtained in Figure 3 since a much smaller force of ~ 1 N was sufficient for flexing, unlike ~ 15 N force that was used in Figure 3c. A flexible MXene/PET-ITO:PET-ITO TENG was used to harvest waste mechanical energy from simple human motions such as the motion of a thumb during texting on a mobile phone (Figures 6-7). Results showed a significant V_{oc} , ranging from -80 to +40 V, which is indeed remarkable considering the fact that other TENGs yield an order of magnitude smaller V_{oc} for similar simple muscle movements (see for example Figure 3 in Kim et al.[50]).

Figure 6. Panels (a) and (b) show the MXene/PET-ITO:PET-ITO TENG mounted on a thumb for harvesting energy from simple human muscle movements. (c) V_{oc} varying between -40 and 70 V was generated by the MXene/PET-ITO:PET-ITO TENG mounted on the thumb. (d) A magnified view of the voltage profile depicted in (c).

Figure 7. A flexible MXene/PET-ITO:PET-ITO TENG mounted on the index finger can harvest waste mechanical energy during typing (a), clicking a mouse (b), or texting on a smart phone (c). V_{oc} generated due to actions in (a-c) are shown in (d-f), which can be as high as -80 V demonstrating the usefulness of flexible MXene/PET-ITO:PET-ITO TENGs for powering wearable and flexible electronics.

In summary, this study demonstrates that in a single-electrode mode configuration with PET-ITO top electrode, the V_{oc} of metallic $Ti_3C_2T_x$ MXene is on par with that of PTFE. In addition, the absence of V_{oc} in a MXene/Glass:PTFE TENG suggests that $Ti_3C_2T_x$ MXene and PTFE have similar electronegativities arising from -F groups in both materials, and can be ranked closely in the triboelectric series. While PTFE-based TENGs exhibit high V_{oc} , they are limited to single-electrode mode configuration due to the poor electrical conductivity of PTFE. In this regard, the metallic $Ti_3C_2T_x$ MXene surmounts this limitation to enable two-electrode mode operation in MXene TENGs without compromising the high V_{oc} observed in PTFE-based TENGs. Using this new triboelectric material, we demonstrated both rigid and flexible TENGs for harnessing useful power in the two-electrode mode configuration. Furthermore, MXene TENGs are flexible, yield significant power and can be integrated into accessories (e.g., wrist bands) or textiles (e.g., elbow or knee patches) to harvest mechanical energy from human activities (e.g., typing, walking) for powering wearable electronics.

Experimental Section

MXene Synthesis: The $\text{Ti}_3\text{C}_2\text{T}_x$ material used in this study was synthesized by selective etching of Al atomic layers from Ti_3AlC_2 by MILD etching method described previously. [36,39,44] In this procedure, 1 g of lithium fluoride (LiF) was added to 20 mL of 6M hydrochloric acid (HCl). 1 g of Ti_3AlC_2 , MAX phase, was slowly added to the LiF/HCl mixture while stirring with a Teflon magnetic stir bar. The reaction was allowed to proceed for 24 hours at 35 °C. After etching, the mixture was washed with deionized water by centrifugation at 3500 rpm for 3 minutes and the acidic supernatant was decanted. The washing process was repeated until a dark supernatant was obtained with a pH ~6. The supernatant was decanted, deionized water was added to the sediment, and the mixture was subjected to manual shaking for 5 minutes to delaminate the $\text{Ti}_3\text{C}_2\text{T}_x$ flakes. The solution was centrifuged for 1 hour at 3500 rpm and the supernatant was used to make thin films (40 nm) of $\text{Ti}_3\text{C}_2\text{T}_x$ for TENG.

Deposition of $\text{Ti}_3\text{C}_2\text{T}_x$: $\text{Ti}_3\text{C}_2\text{T}_x$ was deposited on substrates using spray coating method, similar to previous reports. [39,46,51] For deposition on glass substrates (MXene/Glass), the substrate was cleaned and hydrophilized with Piranha solution (3:1 concentrated sulfuric acid/hydrogen peroxide ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) volume ratio) by sonicating the glass substrates in the solution for 1 hour (Branson Ultrasonic Cleaner, 40 kHz). After the treatment, the glass substrates were washed with deionized water several times and dried under N_2 gas. For deposition on PET-ITO (MXene/PET-ITO), the substrates were used as-received. The aqueous solution of delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ (2.5 mg/mL concentration) was sprayed onto the glass or PET-ITO substrates by airbrush (0.5 mm nozzle, Master Airbrush, G-233, USA). An air dryer (Master Heat Gun, HG-201A, USA) was used to dry the sample between spray coating cycles. After deposition, the substrates were dried in a desiccator for 12 hours before transferring them to a dry glove box, where they were stored until TENG devices were fabricated.

Device fabrication and characterization: We used commercially available ITO coated PET (PET-ITO procured from Sigma-Aldrich, surface resistivity 60 Ω/sq) as the top electrode (Figure 1) while $\text{Ti}_3\text{C}_2\text{T}_x$ coated on glass (MXene/Glass) and PET-ITO (MXene/PET-ITO with $\text{Ti}_3\text{C}_2\text{T}_x$ coated on PET side) served as the bottom electrode in the MXene TENGs ($2.5 \times 5 \text{ cm}^2$). Four pyrex insulating spacers ($5 \times 5 \text{ mm}^2$), cut from a microscope slide, were used to separate the electrodes with an airgap of 1 mm (see Figure 1b). Cu wires were attached to the ITO side of both electrodes (Figures 1c-e) for drawing electrical current from the TENG. The electrical performance of MXene TENG was characterized using a periodic vertical pushing force of $\sim 15 \text{ N}$ (2 Hz), applied by a home-built motorized impactor. [47] All the electrical measurements were obtained using Yokogawa DL 9710L digital oscilloscope.

Supporting Information

Supporting Information is available online or from the author.

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