

Communication

MXene electrochemical microsupercapacitor integrated with triboelectric nanogenerator as a wearable self-charging power unit

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ABSTRACT

The development of miniaturized, wearable, and implantable electronics has increased the demand for small stand-alone power modules that have steady output and long life-time. Given the limited capacity of energy storage devices, one promising solution is to integrate energy harvesting and storage materials to efficiently convert ambient mechanical energy to electricity for direct use or to store the harvested energy by electrochemical means. Here, a highly compact self-charging power unit is proposed by integrating triboelectric nanogenerator with MXene-based microsupercapacitors in a wearable and flexible harvester-storage module. The device can utilize and store the random energy from human activities in a standby mode and provide power to electronics when active. As a result, our microsupercapacitor delivers a capacitance of 23 mF/cm² with 95% capacitance retention after 10,000 charge-discharge cycles, while the triboelectric nanogenerator exhibits a maximum output power of 7.8 μW/cm². Given the simplicity and compact nature, our device can be integrated with a variety of electronic devices and sensors.

1. Introduction

With the rapid development of miniaturized microelectronics, there is an increasing demand for portable or implanted microsystems in various applications [1] such as wearable sensors [2], epidermal electronics [3] and nanorobotics [4]. As a result, developing power units that can power such devices has become significantly important. Recently, triboelectric nanogenerator (TENG), which relies on the coupling effect of contact electrification and electrostatic induction, was invented and has been regarded as a promising technology for harvesting ambient mechanical energy [5–9]. However, the pulsed AC signal as well as low current output makes TENG not suitable for driving microelectronics directly [2]. Alternatively, an energy storage device can be used to store the energy generated by TENGs, so that a self-charging power unit can be formulated. Thin-film or micro-batteries can be used as small-scale energy storage units, but they often suffer from low power density and limited cycle life. Besides, a battery should ideally be charged with constant voltage, which is not directly compatible with TENGs. Meanwhile, miniaturized or integrated electrochemical capacitors, also called microsupercapacitors (MSCs), can

offer a higher power density and longer cycle life than microbatteries due to rapid electron-ion kinetics and sustainable electrode materials. The high rate capability and response speed makes MSCs excellent candidates to be integrated with TENG as energy storage units.

Carbon based materials such as activated carbon [10], onion like carbon [11], carbon nanotubes (CNTs) [12] and carbide-derived carbon [13] have been explored as electrodes for MSCs. These materials store charge via formation of the electrical double layer at the electrode/electrolyte interface, and they are known for their high power density yet low energy density, which is limited by the electrochemical active surface area of the electrodes. In contrast, pseudocapacitors employing metal oxides/sulfides [14,15] or conducting polymers [16–18], utilize fast surface redox reactions and therefore can potentially provide higher energy densities at similar power densities as compared with electrochemical double layer capacitor (EDLC). Recently, two-dimensional layered transitional metal carbides, carbonitrides and nitrides (referred to as MXenes) have gained much attentions as a promising pseudocapacitive electrode materials for energy storage applications. One of the most promising MXene compounds for energy storage is Ti₃C₂T_x, which has shown a stable specific volumetric capacitance close

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to 1500 F/cm³ and 380 F/g (3 μm hydrogel electrode) [19], exceeding that of all carbon-based materials. Besides, the metallic conductivity (~6700 S/cm) [20] of Ti₃C₂T_x MXene facilitates the electronic transport for the redox reactions and thus minimize the self-discharge effect. The high electrical conductivity of Ti₃C₂T_x MXene also eliminates the need for noble metal current collectors, which involves costly deposition processes. Given its 2D layered morphology, MXene is also convenient for flexible energy storage with good mechanical property and strain-tunability, which gives it more versatility to be integrated with other components.

Different methods to integrate TENGs with supercapacitors have been proposed [2,21–27], however, most of these methods suffer from drawbacks. For example, TENGs working in contact-separation mode usually need a spacer, which makes it difficult to fabricate integrated and compact devices. On the other hand, the liquid electrolyte in conventional supercapacitors will evaporate if exposed to air, thus proper encapsulation of the supercapacitor is required, which makes the TENG-supercapacitor device bulky. Furthermore, the TENG and supercapacitors are usually made as two separate parts, so external wiring for electrical connection is needed, which adds extra volume to the system.

Here, we propose a simple technique to fabricate a flexible self-charging power unit, which integrates a single-electrode-mode TENG device with 2D MXene-based solid-state microsupercapacitor into a single monolithic device with silicone rubber as encapsulation material. Our device could simultaneously and effectively convert and store mechanical energy of human biomechanical motions into electrochemical energy. In addition, our device can have a long lifetime for continuous energy harvesting and storage, which can be useful for powering electronics without additional power sources.

2. Results and discussion

Recently, MXene-based MSCs fabricated by employing a Meyer coating and spray-coating methods followed by a direct laser cutting process were reported [28,29]. However, MXene tends to be easily oxidized at high temperatures, and laser engraving was shown to easily oxidize the edge of the interdigitated MXene fingers. To solve this problem, we have proposed a simple one-step method to make the MSC by pre-patterning the substrate. The schematic in Fig. 1(a) shows the details of this process. We first use a CO₂ laser to smoothly cut the PET substrate into the desired pattern, then use direct spray-coating of MXene on the pattern to form the active material pattern; this is followed by painting of the cross-linked gel electrolyte over the entire device to complete the solid-state MSC fabrication. Raman spectroscopy and XRD were used to characterize the active MXene material. As shown in Fig. S1(a), The Raman spectrum of Ti₃C₂T_x exhibits strong peaks at 200 and 722 cm⁻¹, which can be assigned to the A_{1g} modes of Ti₃C₂O₂; the additional peaks at 286, and 630 cm⁻¹ can be assigned to the following vibrational modes: E_g of Ti₃C₂(OH)₂, and E_g of Ti₃C₂F₂, respectively [30]. These peaks reveal the presence of -OH, -O and -F functional groups on Ti₃C₂T_x MXene surface. As compared with PET substrate, Ti₃C₂T_x on PET shows strong (002) XRD peak located at 2θ = 7.2° with FWHM = 0.55°, with corresponding to a d-spacing of 1.2 nm (see Fig. S1(b)). The SEM image in Fig. S1(c) shows that Ti₃C₂T_x electrodes have been uniformly coated on the substrate which is confirmed in the cross-section SEM image (Fig. S1(d)).

Electrochemical performance of Ti₃C₂T_x MXene-based MSC devices was studied by employing polyvinyl alcohol (PVA)/H₃PO₄ gel electrolyte in the two-electrode configuration. The hydrogel electrolyte was produced by incorporating glutaraldehyde (GA) as a crosslinking reagent to form a connection with multiple junction zones. The chemically cross-linked polyvinyl alcohol PVA/H₃PO₄ hydrogel not only serves as the solid-state electrolyte, but also guarantees the structural integrity and mechanical strength of the assembled device [31]. The chemically cross-linked hydrogel shows excellent elasticity and high

ionic conductivity due to a larger water content absorbed in the polymer matrix that helps in fine-tuning ionic conductivity. In addition, it slows down self-discharge of the microsupercapacitors. The CVs of our MSC devices are shown in Fig. 1(b), where symmetric and rectangular curves are observed in the potential window of 0.6 V, indicating good capacitive performance. Since the device was fabricated on flexible substrates, it can be repeatedly bent at various angles and frequencies (Fig. 1(h)) without compromising performance. As shown in Fig. 1(c), the CD profiles obtained at different current densities (0.3–1 mA/cm²) are quite linear in the potential window of 0–0.6 V. Moreover, the IR-drop of the devices was found to be only 0.07 V at a current density of 1 mA/cm². Since no current collectors were used in making these devices, these results show that the MXene electrodes have low intrinsic resistance (5000 S/cm by four-point probe). The calculated areal capacitance based on the discharge curve is shown in Fig. 1(d). Our devices show an energy density of 2.8 mWh/cm³ at a power density of 225 mW/cm³, and an energy density of 2.3 mWh/cm³ at a power density of 744 mW/cm³, which is superior to other state-of-the-art microsupercapacitors (Fig. 1(e)) [12,32–34]. This solid-state MSC exhibits good cycling stability with a capacitance retention up to 76% and coulombic efficiency of 95% over 10k cycles as shown in Fig. 1(f). The self-discharge behavior of the supercapacitor is an important parameter for practical applications, especially when charging at low currents. We investigated the self-discharge behavior of our device via measuring the open circuit potential of the device after thoroughly charging it, and a slow self-discharge rate of 0.1 V/h is observed for the device, which is shown in Fig. 1(g). For real applications, energy storage units are usually packaged in series to supply sufficient voltage. Thus, tandem devices connected in series were examined. The voltage window increases to 2.4 V at the expense of the decreased capacitance. As shown in Fig. 1(i), the CV curves exhibit rectangular shapes even when the voltage window is extended, which is consistent with the nearly ideal triangular CD curves shown in Fig. 1(j).

A single-electrode mode TENG based on carbon-fiber-embedded silicone was designed for integration with the silicone-encapsulated MXene-based MSC. The use of carbon fiber electrode is more cost-effective than previously reported devices based on silver nanowires [35,36]; in addition, carbon fiber retains the advantages of flexibility, ease of fabrication and durability. The adoption of the single-electrode mode eliminates the need of spacer in the contact-separation mode and greatly facilitates the integration of the TENG and MSC in a sealed thin-film manner. The detailed working principle of the TENG device is illustrated in Fig. 2(a–d). Firstly, positive and negative charges are induced on the surfaces of human skin and silicone respectively when they are in contact. Once the positively charged skin leaves the TENG device, the potential of the carbon fiber embedded beneath the negatively charged silicone will decrease in reference to the ground potential, and thus a potential difference will be generated across the two inputs of the bridge rectifier and electrons will flow out from the carbon fiber to charge the supercapacitor. The process continues until the skin reaches the maximum separation distance. In contrast, as the skin re-approaches the TENG, the potential on the carbon fiber will increase and the electrons will flow back to the carbon fiber, which will also charge the supercapacitor through the bridge rectifier. The entire process reverts to the initial state once the skin touches the TENG again. The performance of the TENG was fully characterized under different load conditions and the results are plotted in Fig. 2(e–h). Under the short-circuit condition, the maximum charge transferred per cycle reached about 4.2 nC/cm², and the peak current was about 0.13 μA/cm² at the working frequency of 1.3 Hz. Meanwhile, the open-circuit voltage was nearly 50 V for a device with an active area of 4 cm². The output power of the TENG connected with various external load resistance was measured and plotted, with the maximum output power of 7.8 μW/cm² at a load resistance of 400 MΩ.

Fig. 3(a) displays the schematic illustration of the detailed device structure. Three main components (current collector for TENG, rectifier

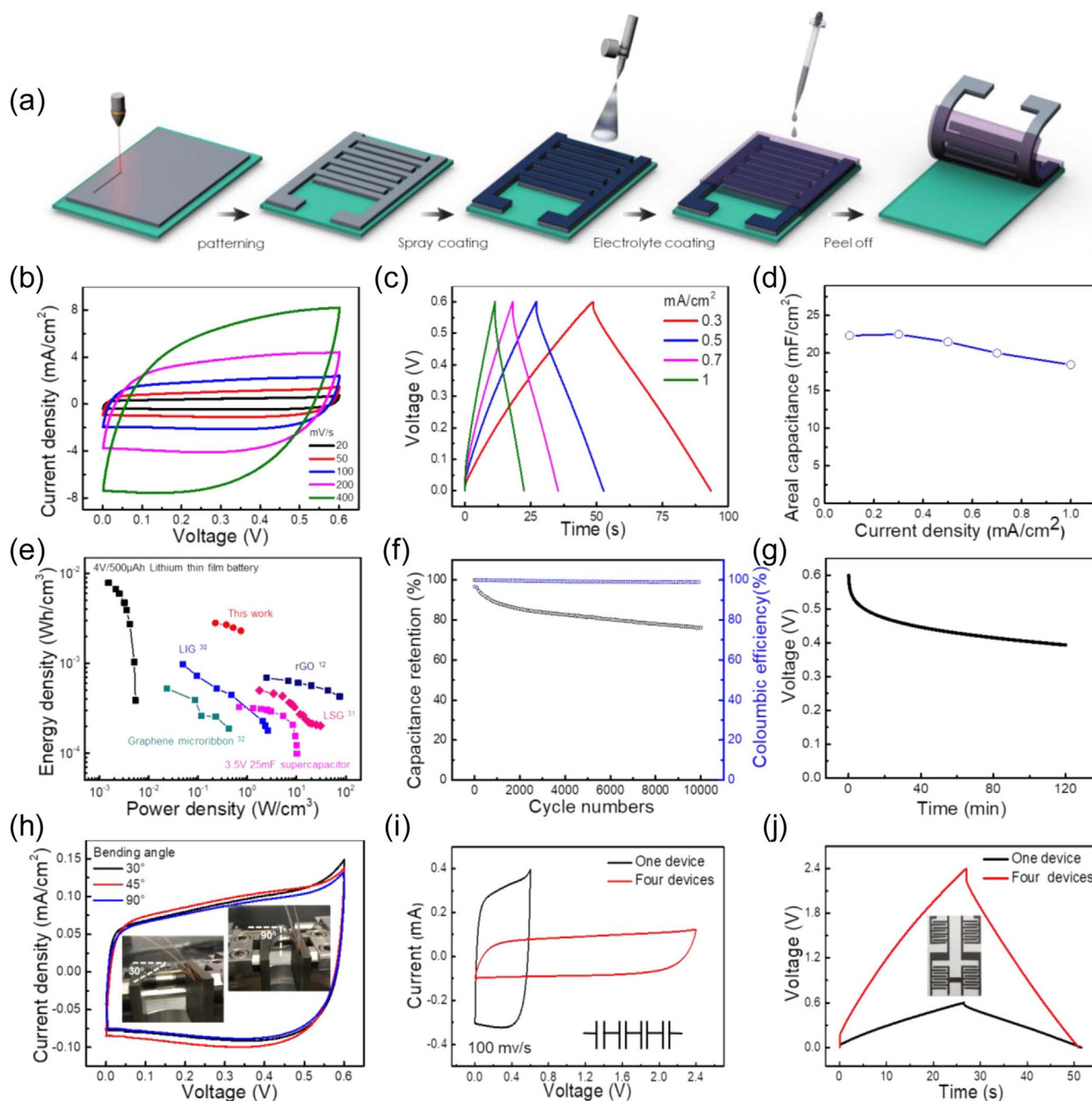


Fig. 1. (a) Schematic illustrating fabrication protocols of $\text{Ti}_3\text{C}_2\text{T}_x$ microsupercapacitors. (b) CV curves at different scan rates (c) Galvanostatic charge-discharge profiles of the device at different current densities. (d) Areal capacitances at different current densities. (e) Ragone plot showing volumetric energy and power densities. (f) Cycling stability and Coulombic efficiency of $\text{Ti}_3\text{C}_2\text{T}_x$ MSC over 10k cycles at a current density of 1 mA/cm^2 . (g) Self-discharge measurement. (h) CV curves for the bent MXene MSC employing gel electrolyte at a scan rate of 50 mV/s , inset shows the digital photographs for the bent configuration of MSC. (i) CV curves at scan rate of 100 mV/s and (j) CD curves at current of 0.4 mA for the integrated tandem supercapacitors.

and microsupercapacitor) were sealed compactly by silicone rubber, while silicone rubber itself serves as both the encapsulating material and stretchable dielectric. Our energy storage device is completely sealed inside the silicone, such that no leakage or evaporation of the electrolyte takes place, thus extending life time for the MSC. Moreover, the mechanical property of the silicone enables the high flexibility of the device as it can undergo different deformations such as fold, twist and stretch (Fig. S2(a–c)), and Kirigami patterns can be introduced into the structure to further increase the stretchability (Fig. S2(d)). Even the silicone rubber tears, solid nature of the electrolytes are not expected to harmfully affect the human body. As shown in Fig. 3(b), the capacitor

can be charged by the regulated current from TENG, which produces electricity when the human skin makes contact with the device. Also, since silicone is a very common material for prosthetic skin, it is biocompatible and provides a comfortable feeling when worn on hand (Inset in Fig. 3(a)).

Several demonstrations of the self-charging power band were conducted to show its possible application scenarios, with the generic equivalent electrical circuit drawn in Fig. 4(a). The power band consists of a TENG as an AC power source, a bridge rectifier as an AC-to-DC converter, and a supercapacitor as an energy storage device. The external load can be connected in parallel to the supercapacitor via a

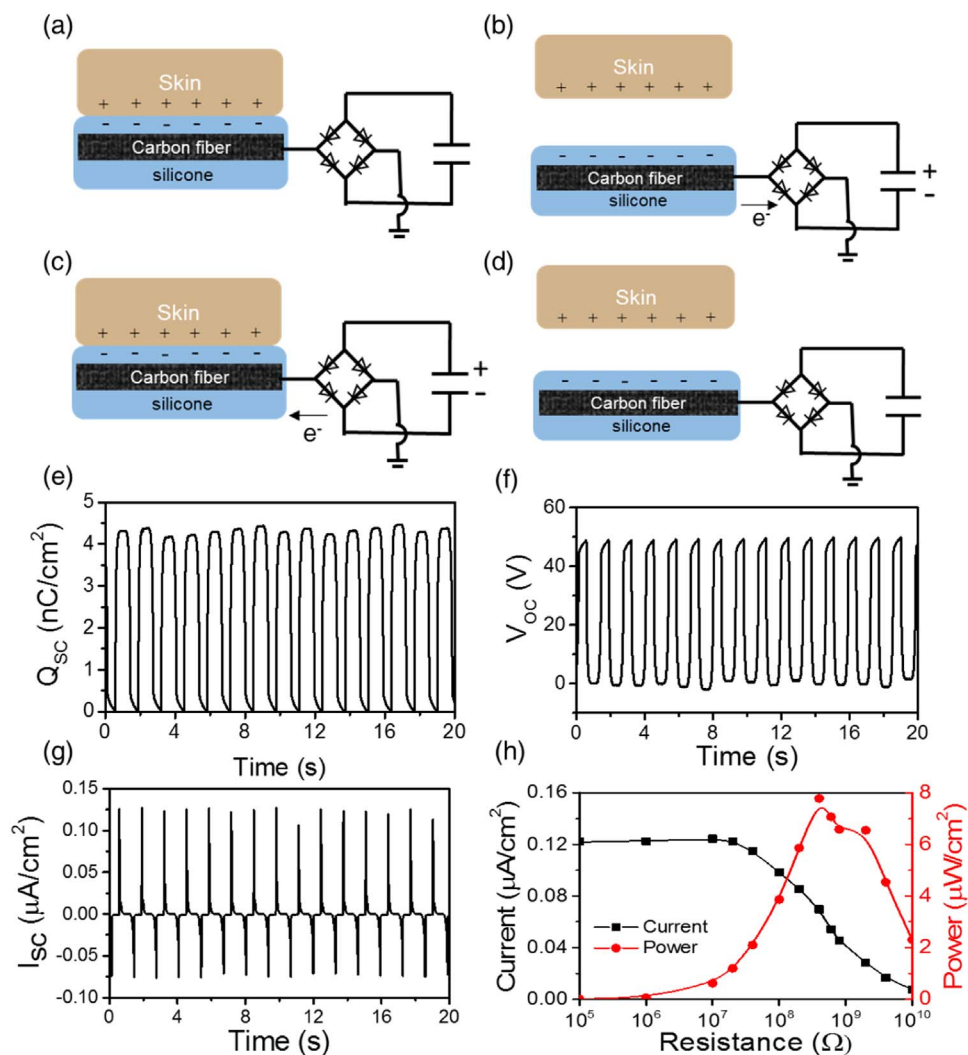


Fig. 2. (a)–(d) Working mechanism of the TENG. (e) Q_{sc} , (f) V_{oc} , and (g) J_{sc} of the triboelectric nanogenerator. (h) Relationship between instantaneous power density and resistance of the external load.

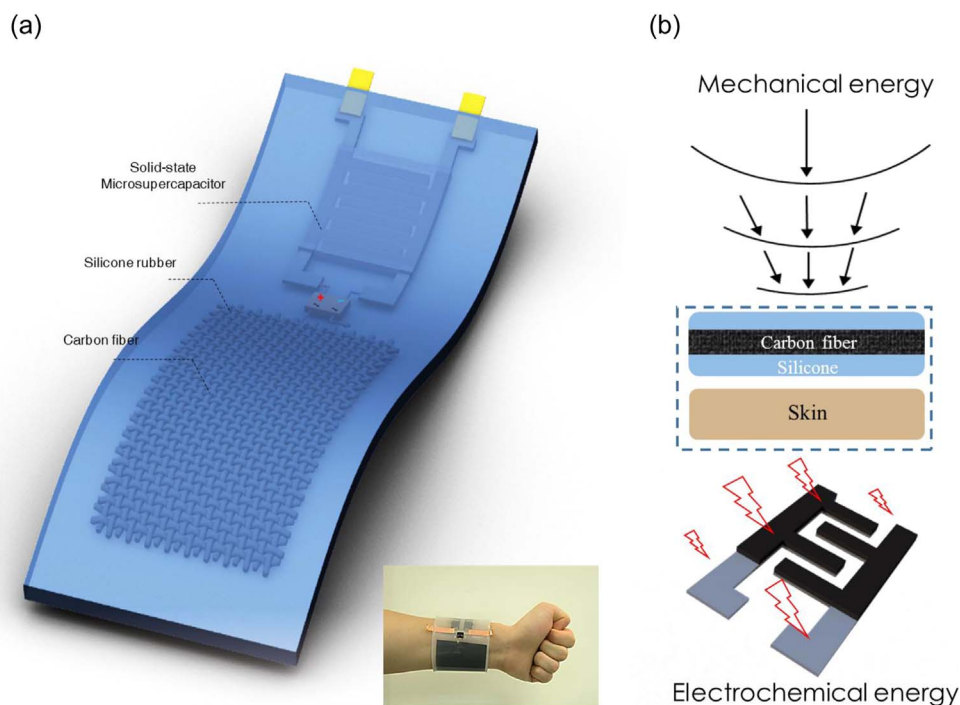


Fig. 3. Wearable self-charging system. (a) Schematic diagram of the whole device, inset photograph demonstrates that the integrated system worn on the forearm. (b) Schematic illustration of mechanism for generating electricity to charge the micro-supercapacitor.

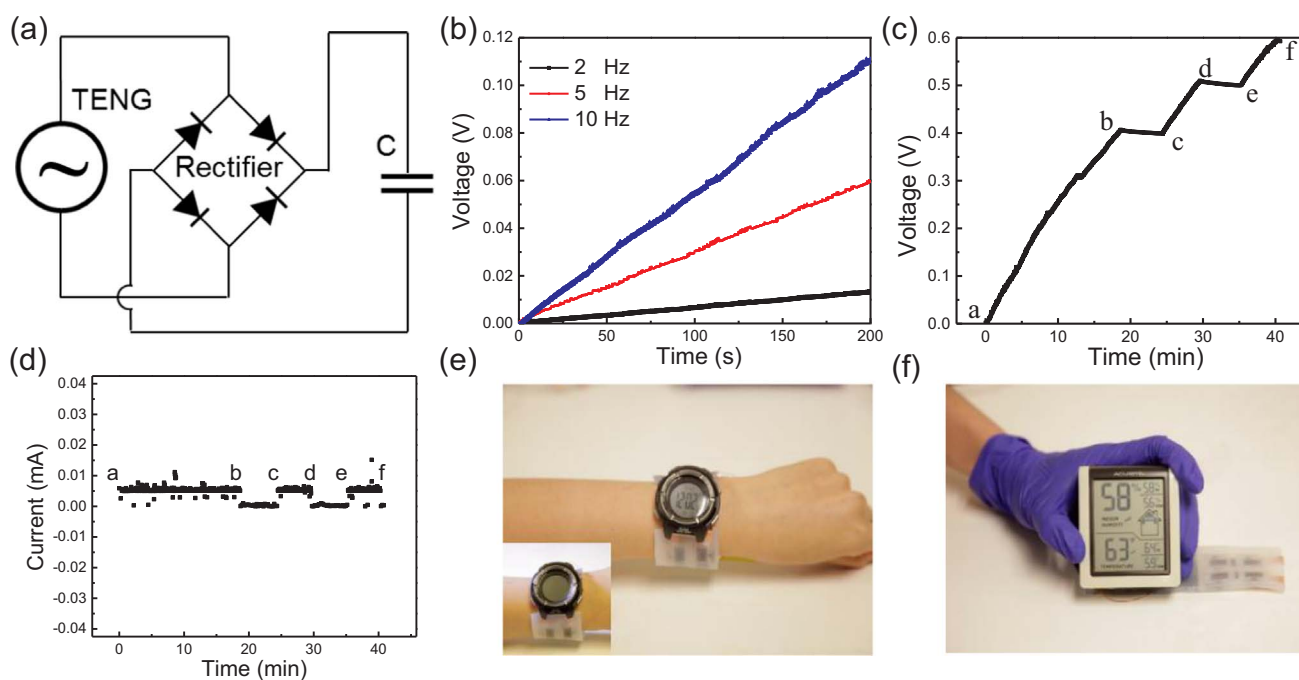


Fig. 4. (a) Circuit diagram of the energy supply mode. (b) Charging curve of the microsupercapacitor charged by TENGs at various frequencies. (c) Charging curve showing the voltage increase of the single capacitor powered by TENG, corresponding current response is shown in (d). Digital photos showing MSC to drive (e) a digital watch and (f) commercial temperature-humidity meter.

switch. Based on the human motion frequency range (1–10 Hz), we have tested the voltage response of our device at different frequencies. As shown in Fig. 4(b), the charging rate of the microsupercapacitor increases when higher frequency is applied to TENG. Especially, under 10 Hz, the MSC can be charged to 0.11 V within 200 s, which demonstrates the fast response even at high frequencies.

Fig. 4(c) illustrates the self-charging capability of the power band (Total capacitance of the series connected capacitor is 4 mF) under hand clapping (the clapping frequency is estimated to be 5 Hz) when no external load was connected. The overall charging curve can be divided into 5 regions: a-b, clapping; b-c: resting; c-d: clapping; d-e: resting; e-f: clapping. It takes roughly 30 min to charge the supercapacitor to 0.6 V when continuously clapping without large current leakage. Corresponding current response of the MSC charged at 5 Hz is shown in Fig. 4(d), where stable current with small fluctuations can be observed at the charging regions. Other body movement such as walking or hand shaking may also be used to charge the nanogenerator. In applications such as wearable sensors where only few readings per day are needed for a few seconds, this energy harvesting rate may be sufficient. However, to demonstrate the feasibility of our flexible power band, we used it to power a watch using four fully-charged MSCs connected in series as shown in Fig. 4(e). The power unit can also power up a thermos-humidity meter (1.5 V) for a few minutes. As in Fig. 4(f), which makes it suitable for both indoor and outdoor activities.

3. Conclusions

We have developed a self-charging power unit by integrating, for the first time, MXene-based microsupercapacitors with a soft and flexible triboelectric nanogenerator, using skin as contact. The power system can be continuously charged by regular human motion (~5 Hz) without significant current leakage. We have also shown the functionality of the system by powering various electronic devices and sensors. Our strategy shows that MXene microsupercapacitors are versatile and can be integrated with energy harvesting devices, which opens new possibilities in wearable/implantable sensor networks.

4. Experimental section

4.1. Synthesis of delaminated $Ti_3C_2T_x$ MXene

All chemicals were used as received without further purification. Layered ternary carbide Ti_3AlC_2 (MAX phase) powder were commercially procured (Carbon-Ukraine Ltd. particle size < 40 μ m). $Ti_3C_2T_x$ MXene was synthesized following minimal intensive layer delamination MILD method by selective etching of aluminum from Ti_3AlC_2 using in situ HF-forming etchant as previously as reported in very detail elsewhere [37]. The etching solution was prepared by adding 1 g lithium fluoride (LiF, Alfa Aesar, 98+ %) to 20 ml 9 M hydrochloric acid (HCl, Fisher, technical grade, 35–38%), followed by stirring for 5 min 1 g of Ti_3AlC_2 powder was slowly added to the MILD etchant at 35 °C and stirred for 24 h. The acidic suspension was washed with deionized (DI) water until pH \geq 6 via centrifugation at 3500 rpm (5 min per cycle) and decanting the supernatant after each cycle. Around pH \geq 6, stable dark green supernatant of $Ti_3C_2T_x$ was observed and then collected after 30 min centrifugation at 3500 rpm. The concentration of $Ti_3C_2T_x$ solution was measured by filtering specific amounts of colloidal solution through a polypropylene filter (3501 Coated PP, Celgard LLC, Charlotte, NC), followed by drying under vacuum at 70 °C overnight.

4.2. Preparation of MXene Microsupercapacitor

Polyethylene Terephthalate (PET) sheets were cleaned with a soap solution to remove surface contamination followed by ultrasonication in isopropanol and DI water sequentially for 5 min each and then dried by blowing nitrogen (N_2) gas. PET patterns were produced by utilizing direct laser machining using a CO_2 Universal Laser Cutter System (model: Professional laser system PLS 6.75, wavelength of 10.6 μ m). The laser power and speed were set to 5% and 30%, respectively. The z-distance between the laser and the sample was 2 cm. AutoCAD technical drawing software was used to design the interdigital finger electrodes at each length of 8 mm, width of 1 mm, and spacing of 1 mm. The laser beam size was 100 μ m. All the laser experiments were performed under ambient conditions. MXene symmetric MSCs were

fabricated by one-step spray-coating of a 4 μm $\text{Ti}_3\text{C}_2\text{T}_x$ film directly onto the PET patterns as the active material. This spray-coated MXene electrode pattern was directly used for fabrication of collector-free microsupercapacitor device by casting the gel electrolyte.

4.3. Preparation of the gel electrolyte

The polyvinyl alcohol (PVA)/ H_3PO_4 gel electrolyte was prepared as follows: 1 g of PVA ($M_w = 89,000\text{--}98,000$, Sigma-Aldrich) was weighed and added into an RB flask containing 10 ml deionized water. The mixture was subsequently heated at 80 $^\circ\text{C}$ with constant stirring until a clear solution was obtained. The solution was then cooled to room temperature and then 0.8 g phosphoric acid (H_3PO_4) was added. It was then stirred for 2 h. After that, the gel was kept in vacuum oven at room temperature for 2 h to remove the extra bubbles in the solution. Before using, the cross-linked gel was made by mixing the as-prepared gel with diluted glutaraldehyde (mass ratio of PVA and glutaraldehyde is 100:1), the whole mixture should be used immediately before it was fully cured.

4.4. Integrating TENG with microsupercapacitor

Acrylic mold was pre-cleaned with ethanol and water, followed by a thin layer of hand soap. Super-soft silicone rubber (Smooth-On, Ecoflex 00–10) was prepared by mixing the two components in a 1:1 vol ratio. The silicone rubber mixture was then casted onto the acrylic plate to form the first layer of silicone. Microsupercapacitor device, rectifier (DF02M, digi-key electronics) and carbon cloth ($4 \times 6 \text{ cm}^2 \times 350 \mu\text{m}$, conductivity 0.1 $\text{m}\Omega \text{ cm}^2$ Fuel Cell store) were placed and aligned on top of the silicone after the bottom silicone had lost its fluidity. Then, another layer of liquid silicone was poured onto the top of them to enclosure the whole device.

4.5. Electrochemical measurements

The electrochemical tests (cyclic voltammetry (CV), galvanostatic charge-discharge (CD), electrochemical cycling stability) were conducted at room temperature using a VMP3 electrochemical workstation (Bio-Logic, France). The electrochemical impedance spectroscopy (EIS) was measured using a Modulab (Solartron Analytical) electrochemical workstation in the frequency range from 100 kHz to 0.01 mHz at open circuit potential by applying a small sinusoidal potential of 10 mV signal. All measurements were done at room temperature.

4.6. Material characterization

X-ray diffraction (XRD) patterns were collected by a Bruker diffractometer (D8 Advance) with $\text{Cu K}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$. The morphology and microstructure of the samples were characterized by a scanning electron microscope (SEM) (Nova Nano 630, FEI) Raman measurements were carried out on the samples using a micro-Raman spectrometer (LabRAM ARAMIS, Horibat-Jobin Yvon) with notch filters cutting at 100 cm^{-1} using a Cobalt laser (633 nm, 5 mW at source). D2 filter (corresponding laser power, 10%) was used to prevent laser induced oxidation during the measurements.

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Supplementary materials

Supporting Information is available from the author.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2018.01.004>.

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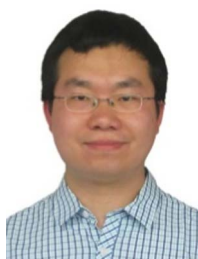
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