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Improved Flexible Triboelectric Nanogenerator Based on Tile-Nanostructure for Wireless Human Health Monitor

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Triboelectric nanogenerators (TENGs) have emerged as promising candidates for integrating with flexible electronics as self-powered systems owing to their intrinsic flexibility, biocompatibility, and miniaturization. In this study, an improved flexible TENG with a tile-nanostructured MXene/polymethyl methacrylate (PMMA) composite electrode (MP-TENG) is proposed for use in wireless human health monitor. The multifunctional tile-nanostructured MXene/PMMA film, which is self-assembled through vacuum filtration, exhibits good conductivity, excellent charge capacity, and high flexibility. Thus, the MXene/PMMA composite electrode can simultaneously function as a charge-generating, charge-trapping, and charge-collecting layer. Furthermore, the charge-trapping capacity of a tile nanostructure can be optimized on the basis of the PMMA concentration. At a mass fraction of 4% PMMA, the MP-TENG achieves the optimal output performance, with an output voltage of 37.8 V, an output current of 1.8 µA, and transferred charge of 14.1 nC. The output power is enhanced over twofold compared with the pure MXene-based TENG. Moreover, the MP-TENG has sufficient power capacity and durability to power small electronic devices. Finally, a wireless human motion monitor based on the MP-TENG is utilized to detect physiological signals in various kinematic motions. Consequently, the proposed performance-enhanced MP-TENG proves a considerable potential for use in health monitoring, telemedicine, and self-powered systems.

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1. Introduction

Miniaturized, integrated, and intelligent flexible electronics have attracted increasing attention owing to their immense potential for health monitoring^[1-3] and metaverse applications.^[4-6]</sup></sup> Thus far, most flexible devices powered by batteries cannot operate sustainably owing to their limited lifespan. Therefore, there is an urgent need to develop self-powered systems. Triboelectric nanogenerators (TENGs), based on Maxwell's displacement current, [7-10] have been demonstrated as an effective energy-harvesting device. TENGs based on different working $modes^{[11-14]}$ can be used to convert ambient energy including human movement,^[15,16] wind,^[17,18] and rain^[19,20] into electrical energy. In addition, their intrinsic flexibility,^[21,22] biocompatibility,^[23,24] and miniaturization^[25,26] make them promising candidates for integrating with flexible electronics as self-powered systems.^[27–30]

To date, various approaches have been proposed to improve the output performance of TENGs, including system design,^[31,32] circuit design,^[33,34] and especially materials design.^[35,36] Materials design is regarded as the most common and effective strategy. A TENG can be divided into

four representative layers: the charge-generating layer, the charge-trapping layer, the charge-collecting layer, and the charge-storage layer.^[37] The charge-generating layer has been investigated extensively, including the surface morphology,^[38] surface functionalization,^[39] charge injection,^[40] and fabrication of new materials.^[41] These methods can increase the surface charge density or facilitate charge transfer. The electrode is usually referred to as the charge-collecting layer. For example, metals^[42] and twodimension materials^[43] with good conductivity and high strength are promising candidates. The charge-trapping layer, which blocks the charge combination, is often overlooked. Electrons can be captured efficiently by incorporating trapping materials into the charge-generating layers. Nanomaterials with a large surface-to-volume ratio, such as MoS₂,^[44] Ag nanowires,^[45] and nanocrystals,^[46] are reported to effectively enhance the output performance. Compared with conventional layered structures, how to integrate the charge-generating and charge-trapping layers, as well as the charge-collecting layer, into a single layer remains a challenge.

MXene is a novel nanomaterial, with excellent properties such as high conductivity,^[47,48] as well as controllable surface state and morphology.^[49–51] Its outstanding properties make it a promising

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candidate for electrodes.^[52] Thus, it can function as an excellent charge-generating or charge-collecting material.^[53–57] However, the lack of an effective charge-trapping layer severely limits the output performance enhancement.

In this work, we first propose a performance-enhanced TENG (MP-TENG) with a multifunctional tile-nanostructured MXene/polymethyl methacrylate (PMMA) layer for use in wireless human health monitors. The tile-nanostructured MXene/PMMA film is self-assembled via vacuum filtration method. Furthermore, because the as-prepared MXene/ PMMA film possesses good conductivity and high flexibility, it can simultaneously function as the charge-generating, charge-trapping, and charge-collecting layer. The tile nanostructure demonstrates excellent charge-trapping capacity, which can be adjusted according to the PMMA concentration. At a mass fraction of 4% PMMA, an optimum output performance of the TENG is obtained with an output voltage of 37.8 V, an output current of 1.8 μ A, and transferred charge of 14.1 nC. The output performance is enhanced over two-fold compared with the pure MXene-based TENG. Moreover, the MP-TENG realizes good power ability and durability to power small electronic devices. Finally, a wireless human motion monitor based on the MP-TENG is used to detect physiological signals in various kinematic joints. The proposed performance-enhanced MP-TENG is shown to have considerable potential for use in health monitoring and telemedicine.

2. Results and Discussion

The construction process of the $Ti_3C_2T_x$ MXene is schematically illustrated in **Figure 1**_a–c. The multi-layer MXene was obtained by chemical stripping of Al atoms from Ti_3AlC_2 using H_2TiF_6 aqueous solution (Figure 1b). In the $Ti_3C_2T_x$ MXene, the surface functional Tx groups play an important role in the electrochemical performance. Then, TMAOH was used as an intercalant to delaminate the multi-layer MXene in order to realize a few-layer MXene (Figure 1c). The PMMA microspheres with a diameter of around 2 μ m were mixed with MXene colloidal solution (Figure 1d). Then, the MXene/PMMA colloi-



Figure 1. Schematic diagram of the MXene/PMMA composite film and MP-TENG. a–c) Fabrication of the few-layer MXene. d–f) Fabrication of the MXene/PMMA composite film. g–i) Fabrication of the laminated MXene/PMMA hybrid film. j) Schematic structure of the MP-TENG. k) Photograph of the MXene/PMMA film. l) Good conductivity of the MXene/PMMA film measured using a digital multimeter.

dal solution was uniformly dispersed at various PMMA concentrations (Figure 1e). Subsequently, the MXene/PMMA solution was self-assembled to form tile nanostructure through vacuum filtration (Figure 1f). The tile nanostructure integrates the charge-generating material and the charge-trapping material into a single layer, which is beneficial for generating and trapping abundant triboelectric charges. The fabrication of the laminated MXene/PMMA through a layer-by-layer method is illustrated in Figure 1g-i. First, a MXene thin film was self-assembled by vacuum filtration (Figure 1g). After drying, filtration of the PMMA film was carried out (Figure 1h). The PMMA microspheres cover the upper surface of the hybrid film (Figure 1i). Subsequently, another MXene film was selfassembled on the PMMA film to form a sandwich structure. The schematic structure of the MP-TENG is displayed in Figure 1j. The filter membrane (polypropylene, PP) supports the electrode film. The MXene/ PMMA electrode acts as a charge-generating layer, chargetrapping layer, and chargecollecting layer. The PDMS and Ag electrode are another chargegenerating layer and chargecollecting layer. A photograph of flexible and free-standing

MXene/PMMA film (30 μ m in thickness) is exhibited in Figure 1k. The flexible electrode demonstrated good conductivity, as shown in Figure 1l, which is advantageous for charge collecting. The relationship between the resistance of MP film and the curvature was shown in Figure S1–S7, Supporting Information.

The morphology and property characterization of the MXene/PMMA thin film are illustrated in **Figure 2**. As shown in Figure 2a, the multilayer $Ti_3C_2T_x$ (lower inset) was obtained by etching Ti_3AlC_2 (Max phase, upper inset). The few-layer $Ti_3C_2T_x$ obtained by delaminating the multi-layer $Ti_3C_2T_x$ is shown in Figure 2b. An SEM image of the PMMA microspheres is exhibited in Figure 2c. It can be clearly seen that the microspheres are uniform with an average diameter of 200 nm. The layered structure and tile nanostructure can be seen in SEM photographs of the lateral section of the MXene/PMMA film. As shown in Figure S2, Supporting Information, the interface between the PMMA film and the MXene film is clear, which indicates that the layered structure was successfully fabricated through the layer-by-layer method. SEM images of the lateral section of the MXene/PMMA hybrid film with different mass fractions of the PMMA microspheres are compared in Figure 2d,f. Evidently, the PMMA microspheres were coated with MXene nanosheets, which formed a tile nanostructure. As the mass fraction of PMMA increases, a tile-nanostructure unit contains more PMMA microspheres. For example, as for the MXene/PMMA hybrid electrode (2% PMMA), the tile nanostructure contains several PMMA microspheres; it basically contains more PMMA microsphere in a unit structure as the mass fraction increase to 4%. However, with a higher mass fraction of PMMA microspheres, the MXene/PMMA solution cannot form a hybrid film through the vacuum filtration method. The as-prepared hybrid films are fragile. The MXene/PMMA hybrid electrodes (8% PMMA and 12% PMMA) were shown in Figure S3, Supporting Information. The five samples were characterized by Fourier transform infrared (FTIR) spectra, as shown in Figure 2g. Several functional groups are commonly observed on the surface of MXenes, including C-F, Ti-C, and Ti-F. Broad absorptions are attributed to



Figure 2. Characteristics of the MXene/PMMA composite film. a) SEM images of the Ti_3AlC_2 particles and multi-layer $Ti_3C_2T_x$. b) SEM image of the fewlayer MXene nanosheet. c) SEM image of the PMMA microspheres. d) SEM image of the lateral section of MXene/PMMA composite film (2% PMMA). e) SEM image of the lateral section of MXene/PMMA composite film (4% PMMA). f) SEM image of the lateral section of the MXene/PMMA composite film (20% PMMA). g) The FT-IR spectra of MXene/PMMA composite films. h) XRD pattern of the Ti3AlC₂ powder and few-layer $Ti_3C_2T_x$ i) Sheet resistances of the MXene/PMMA film with different mass fractions of PMMA.

C-H, Ti-OH/Ti-O-Ti, and C-O/Ti-O, respectively. It is worth noting that C=O (1746 cm⁻¹) bond from PMMA was found in the MXene/ PMMA hybrid electrodes. The XRD spectra in Figure 2h are consistent with the SEM images in Figure 2a,b. The disappeared peaks of Ti₃AlC₂ and the emergence of a characteristic peak of few-layer Ti₃C₂T_x demonstrated that the few-layer Ti₃C₂T_x was successfully realized. The resistances comparison of MXene/PMMA electrode with various mass fractions of PMMA is displayed in Figure 2i. It is evident that the resistance increases with the mass fraction of PMMA. The MXene indicates a minimum sheet resistance of 26 Ω sq⁻¹. In addition, the surface morphology characterized in Figure S4, Supporting Information implies that the MXene/PMMA electrode was relatively flat. And the X-ray photoelectron spectroscopy (XPS) was characterized to evaluate the stability. As shown in Figure S5, Supporting Information, the oxygen peak intensity of MXene film rarely changed after 3 months, which demonstrated the potential for long-term application.

Based on the excellent electrical and mechanical performance of the MXene/PMMA hybrid electrode, a flexible contact-separating mode MP-TENG was constructed. The working mechanism of this TENG is illustrated in Figure 3a. In the original state (i), the two triboelectric layers are fully separated, and there is no triboelectric charge. Under an external compressive force, the MXene/PMMA film and PDMS film are in complete contact, and equal amounts of positive and negative charges are induced on the two triboelectric layers (ii). The distance between the two layers gradually increases as the force is released, and the potential difference between the MXene/ PMMA electrode and the Ag electrode drives the electron transfer from the Ag electrode to the MXene/PMMA electrode (iii). Then, the distance between the two layers reaches the maximum value, and there is no charge transfer charges (iv). Next, when the PDMS film approaches the MXene/PMMA electrode, the opposite potential difference will result in opposite electron flow (v). Finally, when the two triboelectric layers are in contact again, the TENG returns to state (ii) and starts a new cycle. The corresponding finite element simulation of the open-circuit voltage is displayed in Figure 3b. In the opencircuit state, there is no charge transfer, and the potential difference is proportional to the distance between the two triboelectric layers.

When the two layers are fully separated, the potential difference reaches the maximum value.

A series of MP-TENGs with different mass fractions of PMMA (0%, 2%, 4%, and 20%) were fabricated to determine the effect of the PMMA on the output performance. The PMMA mass ratio of the MXene/PMMA film was investigated to increase the output performance. For convenience, the MP-TENGs based on the four aforementioned PMMA mass fractions are marked as P-0, P-2, P-4, and P-20. respectively. And these devices were measured under a force of 50 N in a frequency of 5 Hz. As compared in Figure 4a-c, the output voltage, output current, and transferred charge of P-0 were 13.0 V, 0.8 µA, and 6.7 nC, respectively. Furthermore, it was obvious that the output performance gradually increased initially, and drastically decreased with the increasing mass fraction of the PMMA microspheres. The P-4 possessed the highest output performance, with an output voltage of 37.8 V, an output current of 1.8 µA, and transferred charge of 14.1 nC. The output performance was enhanced over twofold compared with P-0. The enhanced output performance is attributed to the charge-trapping capacity of the tile nanostructure. It is worth noting that the output performance significantly decreased when the PMMA concentration increased from 4% to 20%. The output performance of P-20 was even lower than that of P-0. The sharp decrease in the output performance is mainly due to the excessive agglomeration of PMMA microspheres, which destroys the tile nanostructure and increases the resistance, thereby weakening the triboelectric charge-generating and the charge-trapping capacity considerably. In addition, the TENG based on the layered MXene/PMMA/MXene film showed an output voltage of 22.3 V, an output current of 1.22 µA, and transferred charge of 10.1 nC. Its output performance lies between those of P-0 and P-2. We ascribe this result to its better charge-trapping ability compared to P-0, but worse charge-trapping ability than that of P-2.

To better understand the output performance, we further investigated the dependence of the output performance on the compressive force and frequency. The relationship between the output performance and the compressive force is shown in Figure 4d–f. These devices operated at a frequency of 2 Hz. When the compressive force was varied from 10 to 50 N, the output performance of all the devices except P-20 increased



Figure 3. Schematic illustration of the working mechanism of the flexible MP-TENG. a) Working mechanism and charge transfer of the MP-TENG with a load resistance. b) The finite element analysis of the potential difference in the open-circuit state.

by various degrees. The output performance of P-20 decreased as the compressive force increased, mainly due to its poor mechanical properties. As we mentioned in Figure S3, Supporting Information, the MXene/PMMA composite film is easily cracked as the mass fraction of PMMA exceeds 8%. Additionally, the effect of the frequency on the output performance is revealed in Figure 4g-i. In general, there were no significant changes in the output voltage and transferred charge, as the frequency increased from 1 to 5 Hz. However, there was a noticeable improvement in the output current with increasing frequency. We can ascribe this phenomenon to faster electron transfer at higher frequencies.



Figure 4. a) The output voltage, b) output current, and c) transferred charge of the MP-TENG with different mass fractions of PMMA microspheres (0%, 2%, 4%, and 20%). d) The output voltage e) output current, and f) transferred charge of the MP-TENGs under various forces (10–50 N, mass fraction of PMMA = 4%). The relationship between the g) output voltage, h) output current, and i) transferred charge of the MP-TENGs and the frequencies.

In order to interpret the phenomenon of the output performance change, the charge distribution and corresponding charge-trapping mechanism with various PMMA mass fractions are schematically illustrated in **Figure 5**. When the PMMA fraction was 0%, a pure MXene electrode was obtained, as shown in Figure 5a. The pure MXene film can rub against the PTFE film, which acts as the charge-generating and charge-collecting layers. The triboelectric charges will easily combine with the induced charges. When the structure is delaminated, the PMMA film is the charge-trapping layer and the two MXene films are the charge-generating and charge-collecting layers, as illustrated in Figure 5b. The triboelectric charge is distributed on the top MXene surface and the induced charge is distributed on the bottom MXene electrode. The middle PMMA layer has a low charge-trapping capacity. As

the PMMA fraction increased to 2%, a tile nanostructure was formed, as exhibited in Figure 5c. This enhances the charge-trapping capacity and decreases the combination between the triboelectric charges and the induced charges. Therefore, a higher output performance is achieved. When the PMMA fraction increases to 4% (Figure 5d), additional tile nanostructures are built regularly. The charge-trapping capacity is further increased, leading to fewer combinations and a higher output performance. However, as the PMMA fraction is substantially increased to 20% (Figure 5e), an effective tile nanostructure cannot be constructed. The chaotic structure will result in excessive charge combination and severe loss. Meanwhile, some PMMA microspheres may remain on the PDMS surface during the contact process. Overall, the output performance is significantly degraded. We also characterized the amount of



Figure 5. Schematic illustration of the charge distribution of the tile-nanostructured MP-TENG and the corresponding charge-trapping mechanism of a) P-0 (0% PMMA), b) MXene/PMMA/MXene, c) P-2 (2% PMMA), d) P-4 (4% PMMA) and e) P-20 (20% PMMA). f–j) Planar average differential potential density by KPFM.

surface charge in each sample by KPFM, as shown in Figure 5f–j. The measured average potentials for MXene, MXene/PMMA/MXene, MXene/PMMA (2%), MXene/PMMA (4%), and MXene/PMMA (20%) were -0.21, -0.19, -0.18, -0.10, and -0.25 V, respectively. According to the measurement method, the surface average potential follows the order: MXene/PMMA (20%) > MXene > MXene/PMMA/MXene > MXene/PMMA (2%) > MXene/PMMA (4%). The differences in surface potential originated from different PMMA ratio. Furthermore, the difference in the surface potential of MXene/PMMA film results in the difference of output performance of MP-TENGs.

The power capacity of the TENG is an important parameter for evaluating its potential applications. Thus, the output performance and charge capacity were investigated, as shown in Figure 6a-c. A TENG with an effective area of 3 cm² was tested under a force of 15 N and a frequency of 1 Hz. First, its output voltage and output current were measured under different load resistances ranging from 10 k Ω to 10 G Ω . Obviously, the output current decreased as the load resistance increased. Nevertheless, the output voltage showed an opposite trend. The instantaneous output power can be calculated by multiplying the output voltage and output current. Thus, the instantaneous output power will reach a maximum value at a certain resistance. As shown in Figure 6b, P-4 achieved a maximum output power of 7.3 μ W at a load resistance of 10 M Ω , which was around 20 times higher than that of P-0. To assess its charge capacity, a series of capacitors with different capacitances were tested. As displayed in Figure 6c, the capacitor (1 μ F) can be charged to 3 V in 100 s, and a 3.3 μ F capacitor was charged to 1 V. Thus, it has promising charge capacity. And the charge-discharge profile of the 2.2 µF capacitor was provided in Figure S6, Supporting Information.

In addition, stability is also an important parameter for assessing its practicality. As shown in Figure 6d, the output voltage remains steady

after the triboelectric charge reaches saturation. There was nearly no performance degradation after ~10 000 cycles, which demonstrates excellent stability. Considering the alternating current (AC) of the TENG, a rectifier circuit and a capacitor were used for AC rectification for subsequent use. The conversion circuit is illustrated in Figure 6e. It is possible to easily light up more than 10 LEDs by tapping the TENG with a finger, as shown in Figure 6f. More importantly, a thermohygrometer can be directly powered by quickly and vigorously striking the TENG, as displayed in Figure 6g. These results provide ample evidence that a TENG-based power supply can power small electronic devices. In addition, the comparison of MXene-based TENG is provided in Table S1–S7, Supporting Information.

To further demonstrate the potential applications of the MP-TENG in sensing and energy harvesting, we assembled a TENG-based wireless transmission system. This wireless transmission system includes a flexible MP-TENG, a lithium-ion battery, a small chip, and a mobile application. The small chip can process the output signal from the MP-TENG and transmit it wirelessly via the mainboard (Bluno Beetle) and Bluetooth module. Then, the signal can be received by the mobile application and displayed on the screen in real time. The photograph of the wireless transmission system was provided in Figure S7, Supporting Information. As illustrated in Figure 7a, the wireless human motion monitor was utilized to detect the following motions: throat pronunciation, belly breathing, finger bending, elbow bending, wrist bending, and finger tapping. First, the flexible MP-TENG was attached to the throat. Different output signals were obtained as a volunteer pronounced the letters "M" "J" and "U", as shown in Figure 7b. Then, it was attached to the belly. It could monitor shallow and deep breathing behavior according to the signal amplitude and frequency, as shown in Figure 7c. Furthermore, it was used for monitoring joint motions such as finger bending and wrist bending. As displayed in Figure 7d-f, the



Figure 6. a) The relationship of the output voltage and output current with the load resistance. b) The relationship between the output power and the load resistance. c) The charging curve of the capacitors with different capacitances ranging from 1 to 22 μ F. d) The stability test of the TENG with 10 000 cycles. e) Schematic of the rectifying circuit. f) 18 red LEDs lighted by tapping the TENG. g) A hygrothermograph powered by the TENG.

signals were all proportional to the bending angle. Apparently, higher output signals were obtained at larger bending angles. It can effectively monitor joint motion, which is advantageous for health monitoring and telemedicine applications. In addition, it can continuously detect finger tapping signals, as shown in Figure 7g.

3. Conclusion

In summary, a flexible MP-TENG enhanced using a multifunctional tile-nanostructured MXene/PMMA film was reported for human energy harvesting and wireless physiological monitoring. The building unit of



Figure 7. a) Schematic of wireless transmission system for human body motion sensing and energy harvesting. The digital photographs show various detected locations corresponding to the blue circles. A mobile application can display the signal in real time. b) Real-time signals for the pronunciation of the letters "M" "J" "U" with the MP-TENG mounted on the throat. c) The output voltage of the MP-TENG mounted on the human belly. d) The real-time monitoring of wrist bending. e) Real-time monitoring of elbow bending. f) The real-time monitoring finger bending. g) Real-time output voltage of the MP-TENG by finger tapping.

the tile nanostructure is a PMMA microsphere and MXene nanosheets, which were self-assembled utilizing vacuum filtration method. Owing to the high conductivity, strong charge-trapping capacity, and high flexibility of the as-obtained MXene/PMMA film, it simultaneously functions as the charge-generating, charge-trapping, and chargecollecting layer in the MP-TENG. Moreover, we can improve the charge-trapping capacity of the MXene/PMMA electrode by adjusting the PMMA concentration, and thus enhance the output performance of the MP-TENG. At a mass fraction of 4% PMMA, an optimum output performance of the TENG is obtained with an output voltage of 37.8 V, an output current of 1.8 µA, and transferred charge of 14.1 nC. Furthermore, the output power was enhanced over 20-fold compared with the pure MXene-based TENG. The MP-TENG realizes good power capacity to power small electronic devices and outstanding stability after 10 000 working cycles. Finally, a wireless monitoring system based on the MP-TENG was demonstrated to detect physiological signals in various kinematic motions such as throat pronunciation, belly breathing, and finger and elbow bending. Consequently, the proposed MP-TENG has a promising prospect in the flexible electronics and self-powered system.

4. Experimental Section

*Preparation of Ti*₃C₂T_x: The multi-layer Ti₃C₂T_x slurry was obtained by chemically etching the Al atoms from Ti₃AlC₂ (XFNANO, ≥90 wt%, MAX phase) using less hazardous H₂TiF₆ aqueous solution. Specifically, 5 mL of H₂TiF₆ (Aladdin, AR, 50 wt%) aqueous solution was diluted with 5 mL deionized water in a 25 mL Teflon beaker. The beaker was then placed in an ice-water bath, and 2 g of Ti₃AlC₂ was gradually added to the solution under vigorous stirring with a Teflon magnetic stir bar for 15 min. The reaction proceeded for 6 h at 60 °C and another 12 h at 30 °C. The slurry was then centrifuged at 960 g for 5 cycles until pH > 6. The few-layer Ti₃C₂T_x colloid was produced by delaminating multi-layer Ti₃C₂T_x was suspended in a mixture of 20 mL of deionized water and 1 mL of TMAOH (25% aqueous solution) at 60 °C for 3 h. In addition, interlayer delamination was achieved by sonication for 1 h, to obtain a stable colloidal solution.

Synthesis of PMMA microspheres: PMMA microspheres were prepared using methyl methacrylate (Aladdin, AR) as a reactant, sodium dodecyl benzene sulfonic acid (SDBS, SCRC, AR) as a surfactant, and potassium persulfate (SCRC, AR) as an initiator. Next, 10 mL of the vacuum distillate (methyl methacrylate) was poured into a 250 mL three-neck flask with 80 mL of distillate water and 10 mL of 0.025-mol L⁻¹ SDBS solution. The mixture was subjected to vigorous stirring at

25 °C for 30 min with a magnetic stir bar in order to obtain a uniform emulsion. Then, 20 mL of aqueous solution containing 0.026 g of potassium persulfate was added into the emulsion dropwise and refluxed at 70 °C for 3 h. Finally, the milk-white PMMA suspension was centrifuged and washed three times to remove SDBS.

Synthesis of PMMA-Ti₃C₂Tx film: A certain amount of the PMMA microsphere suspension was mixed with Ti₃C₂T_x colloidal solution at 60 °C for 5 min. The concentrations of the MXene and PMMA solutions used in this work were 2 and 1 mg mL⁻¹, respectively. Then, vacuum-assisted filtration was carried out to fabricate the Ti₃C₂T_x/PMMA film. The Ti₃C₂T_x/PMMA multilayer film was produced by filtrating and drying the raw materials in the following order: Ti₃C₂T_x PMMA-Ti₃C₂T_x ithus, a sandwich-like structure was formed.

Construction of flexible MP-TENG: First, Polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) solution was spin-coated to form a dielectric layer with a thickness of 0.5 mm. Then, a 50-nm-thick Ag layer was deposited on the plasmatreated PDMS using vacuum sputter coater (DP650, France) to form the top electrode. The MXene/PMMA film was prepared utilizing the aforementioned method. The two films were attached using four PDMS cubes with a gap distance of 2 mm to form a flexible MP-TENG. The effective contact area of the TENG was around 7 cm². For convenience, the MP-TENGs based on the four aforementioned PMMA mass fractions are marked as P-0, P-2, P-4, and P-20, and the asprepared MXene/PMMA/MXene film is marked as 2% PMMA multilayer.

Characterization and measurements: Scanning electron microscopy (SEM) and energy-dispersive spectroscopy images were acquired using a field-emission SEM (SU8010, Hitachi, Japan). Kelvin probe force microscopy (KPFM) was conducted by Dimension Icon (Bruker). The Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Bruker Tensor) instrument was applied to detect the physical interactions of samples by VERTEX 80v. X-ray photoelectron spectroscopy (XPS) was conducted using a PHI-5000 VersaProbe II (ULVAC-PHI) instrument with monochromatic AI K α radiation. The X-ray diffraction (XRD) patterns were measured by a diffractometer (MiniFlex600, Rigaku, Japan). The surface morphology was measured using a 3D laser scanning microscope (VK-X200 series). A linear motor positioning system (SBT951-T, SIMBATOUCH, China) was used to control the forces, frequencies, and working distances. The resistance and the output electric performance were recorded using a digit multimeter (DMM 6500) and an electrometer (Keithley 6514, American), respectively.

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Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Keywords

flexible electrode, MXene, tile nanostructure, triboelectric nanogenerator, wireless monitor

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- [1] J. Dai, L. Li, B. Shi, Z. Li, Biosens. Bioelectron. 2021, 194, 113609.
- [2] Y. Wu, Y. Li, Y. Zou, W. Rao, Y. Gai, J. Xue, L. Wu, X. Qu, Y. Liu, G. Xu, L. Xu, Z. Liu, Z. Li, Nano Energy 2022, 92, 106715.
- [3] Y. Ma, Y. Zhang, S. Cai, Z. Han, X. Liu, F. Wang, Y. Cao, Z. Wang, H. Li, Y. Chen, X. Feng, Adv. Mater. 2020, 32, 1902062.
- [4] J. J. Kim, Y. Wang, H. Wang, S. Lee, T. Yokota, T. Someya, Adv. Funct. Mater. 2021, 31, 2170286.
- [5] X. Yu, Z. Xie, Y. Yu, J. Lee, A. Vazquez-Guardado, H. Luan, J. Ruban, X. Ning, A. Akhtar, D. Li, B. Ji, Y. Liu, R. Sun, J. Cao, Q. Huo, Y. Zhong, C. Lee, S. Kim, P. Gutruf, C. Zhang, Y. Xue, Q. Guo, A. Chempakasseril, P. Tian, W. Lu, J. Jeong, Y. Yu, J. Cornman, C. Tan, B. Kim, K. Lee, X. Feng, Y. Huang, J. A. Rogers, *Nature* **2019**, *575*, 473.
- [6] J. D. N. Dionisio, W. G. Burns III, R. Gilbert, ACM Comput. Surv. 2013, 45, 34.
- [7] F.-R. Fan, Z.-Q. Tian, Z. Lin Wang, Nano Energy 2012, 1, 328.
- [8] Z. L. Wang, Mater. Today 2017, 20, 74.
- [9] Z. L. Wang, Nano Energy 2020, 68, 104272.
- [10] Y. Chen, Y. Jie, N. Wang, Z. L. Wang, X. Cao, Nano Energy 2020, 76, 105051.
- [11] F. R. Fan, L. Lin, G. Zhu, W. Wu, R. Zhang, Z. L. Wang, Nano Lett. 2012, 12, 3109.
- [12] G. Zhu, J. Chen, Y. Liu, P. Bai, Y. S. Zhou, Q. Jing, C. Pan, Z. L. Wang, Nano Lett. 2013, 13, 2282.
- [13] Y. Yang, H. Zhang, J. Chen, Q. Jing, Y. S. Zhou, X. Wen, Z. L. Wang, ACS Nano 2013, 7, 7342.
- [14] S. Wang, Y. Xie, S. Niu, L. Lin, Z. L. Wang, Adv. Mater. 2014, 26, 2818.
- [15] C. Wang, X. Qu, Q. Zheng, Y. Liu, P. Tan, B. Shi, H. Ouyang, S. Chao, Y. Zou, C. Zhao, Z. Liu, Y. Li, Z. Li, ACS Nano 2021, 15, 10130.
- [16] Z. Zhao, C. Yan, Z. Liu, X. Fu, L. M. Peng, Y. Hu, Z. Zheng, Adv. Mater. 2016, 28, 10267.
- [17] J. Bae, J. Lee, S. Kim, J. Ha, B. S. Lee, Y. Park, C. Choong, J. B. Kim, Z. L. Wang, H. Y. Kim, J. J. Park, U. I. Chung, *Nat. Commun.* **2014**, *5*, 4929.
- [18] Y.-C. Lai, Y.-C. Hsiao, H.-M. Wu, Z. L. Wang, Adv. Sci. 2019, 6, 1801883.
- [19] H. Chen, C. Xing, Y. Li, J. Wang, Y. Xu, Sustain. Energy Fuels 2020, 4, 1063.
- [20] W. Xu, H. Zheng, Y. Liu, X. Zhou, C. Zhang, Y. Song, X. Deng, M. Leung, Z. Yang, R. X. Xu, Z. L. Wang, X. C. Zeng, Z. Wang, *Nature* **2020**, 578, 392.
- [21] H. Chen, W. Yang, C. Zhang, M. Wu, W. Li, Y. Zou, L. Lv, H. Yu, H. Ke, R. Liu, Y. Xu, J. Wang, Z. Li, *Nano Res.* **2022**, *15*, 2465.
- [22] S. A. Khan, H. L. Zhang, Y. Xie, M. Gao, M. A. Shah, A. Qadir, Y. Lin, Adv. Eng. Mater. 2017, 19, 1600710.
- [23] S. Parandeh, M. Kharaziha, F. Karimzadeh, Nano Energy 2019, 59, 412.
- [24] J. Ma, J. Zhu, P. Ma, Y. Jie, Z. L. Wang, X. Cao, ACS Energy Lett. 2020, 5, 3005.
- [25] C. Chen, Z. Wen, J. Shi, X. Jian, P. Li, J. T. W. Yeow, X. Sun, Nat. Commun. 2020, 11, 4143.
- [26] Q. Wang, M. Chen, W. Li, Z. Li, Y. Chen, Y. Zhai, Nano Energy 2017, 41, 128.
- [27] Y. Su, G. Chen, C. Chen, Q. Gong, G. Xie, M. Yao, H. Tai, Y. Jiang, J. Chen, Adv. Mater. 2021, 33, 2101262.
- [28] J. Qin, X. Yang, C. Shen, Y. Chang, Y. Deng, Z. Zhang, H. Liu, C. Lv, Y. Li, C. Zhang, L. Dong, C. Shan, *Nano Energy* **2022**, 101, 107549.
- [29] J. Sun, Y. Chang, J. Liao, S. Chang, S. Dai, Y. Shang, C. Shan, L. Dong, Nano Energy 2022, 99, 107392.
- [30] J. Zhao, Y. Xiao, W. Yang, S. Zhang, H. Wang, Q. Wang, Z. Sun, W. Li, M. Gao, Z. Wang, Y. Xu, H. Chen, J. Wang, *Adv. Mater. Technol.* **2023**, 8, 2201769.
- [31] W. Yang, J. Chen, Q. Jing, J. Yang, X. Wen, Y. Su, G. Zhu, P. Bai, Z. L. Wang, Adv. Funct. Mater. 2014, 24, 4090.
- [32] D. Yoo, S. Lee, J.-W. Lee, K. Lee, E. Y. Go, W. Hwang, I. Song, S. B. Cho, D. W. Kim, D. Choi, J.-Y. Sim, D. S. Kim, *Nano Energy* **2020**, 69, 104388.
- [33] S. Niu, X. Wang, F. Yi, Y. S. Zhou, Z. L. Wang, Nat. Commun. 2015, 6, 8975.

- [34] C. Shan, W. Liu, Z. Wang, X. Pu, W. He, Q. Tang, S. Fu, G. Li, L. Long, H. Guo, J. Sun, A. Liu, C. Hu, *Energy Environ. Sci.* **2021**, *14*, 5395.
- [35] W.-T. Cao, H. Ouyang, W. Xin, S. Chao, C. Ma, Z. Li, F. Chen, M.-G. Ma, Adv. Funct. Mater. 2020, 30, 2004181.
- [36] D. Y. Xie, Q. Ma, H. Qi, X. Liu, X. Chen, Y. Jin, D. Li, W. Yu, X. Dong, Nanoscale 2021, 13, 19144.
- [37] D. W. Kim, J. H. Lee, J. K. Kim, U. Jeong, NPG Asia Mater. 2020, 12, 6.
- [38] H. Chen, L. Bai, T. Li, C. Zhao, J. Zhang, N. Zhang, G. Song, Q. Gan, Y. Xu, Nano Energy 2018, 46, 73.
- [39] H. Y. Li, L. Su, S. Y. Kuang, C. F. Pan, G. Zhu, Z. L. Wang, Adv. Funct. Mater. 2015, 25, 5691.
- [40] S. Wang, Y. Xie, S. Niu, L. Lin, C. Liu, Y. S. Zhou, Z. L. Wang, Adv. Mater. 2014, 26, 6720.
- [41] M. Seol, S. Kim, Y. Cho, K.-E. Byun, H. Kim, J. Kim, S. K. Kim, S.-W. Kim, H.-J. Shin, S. Park, Adv. Mater. 2018, 30, 1801210.
- [42] A. S. M. I. Uddin, P. S. Kumar, K. Hassan, H. C. Kim, Sens. Actuators B Chem. 2018, 258, 857.
- [43] S. Kim, M. K. Gupta, K. Y. Lee, A. Sohn, T. Y. Kim, K. S. Shin, D. Kim, S. K. Kim, K. H. Lee, H. J. Shin, D. W. Kim, S. W. Kim, Adv. Mater. 2014, 26, 3918.
- [44] C. Wu, T. W. Kim, J. H. Park, H. An, J. Shao, X. Chen, Z. L. Wang, ACS Nano 2017, 11, 8356.
- [45] S. Cheon, H. Kang, H. Kim, Y. Son, J. Y. Lee, H.-J. Shin, S.-W. Kim, J. H. Cho, Adv. Funct. Mater. 2018, 28, 1703778.

- [46] R. Wen, J. Guo, A. Yu, J. Zhai, Z. I. Wang, Adv. Funct. Mater. 2019, 29, 1807655.
- [47] M. Ghidiu, M. R. Lukatskaya, M.-Q. Zhao, Y. Gogotsi, M. W. Barsoum, *Nature* 2014, 516, 78.
- [48] K. Ghosh, M. Pumera, Small Methods 2021, 5, 2100451.
- [49] Q. Wei, G. Chen, H. Pan, Z. Ye, C. Au, C. Chen, X. Zhao, Y. Zhou, X. Xiao, H. Tai, Y. Jiang, G. Xie, Y. Su, J. Chen, Small Methods 2022, 6, 2101051.
- [50] H. An, T. Habib, S. Shah, H. Gao, M. Radovic, M. J. Green, J. L. Lutkenhaus, Sci. Adv. 2018, 4, eaaq0118.
- [51] H. Jing, H. Yeo, B. Lyu, J. Ryou, S. Choi, J.-H. Park, B. H. Lee, Y.-H. Kim, S. Lee, ACS Nano 2021, 15, 1388.
- [52] Y. Gao, G. Liu, T. Bu, Y. Liu, Y. Qi, Y. Xie, S. Xu, W. Deng, W. Yang, C. Zhang, Nano Res. 2021, 14, 4833.
- [53] Z. Zhang, Q. Yan, Z. Liu, X. Zhao, Z. Wang, J. Sun, Z. L. Wang, R. Wang, L. Li, Nano Energy **2021**, 88, 106257.
- [54] D. Wang, D. Zhang, Y. Yang, Q. Mi, J. Zhang, L. Yu, ACS Nano 2021, 15, 2911.
- [55] D. Wang, D. Zhang, P. Li, Z. Yang, Q. Mi, L. Yu, Nanomicro Lett. 2021, 13, 57.
- [56] X. Luo, L. Zhu, Y.-C. Wang, J. Li, J. Nie, Z. L. Wang, Adv. Funct. Mater. 2021, 31, 2104928.
- [57] Y. Dong, S. S. K. Mallineni, K. Maleski, H. Behlow, V. N. Mochalin, A. M. Rao, Y. Gogotsi, R. Podila, *Nano Energy* **2018**, 44, 103.