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## High-voltage asymmetric MXene-based on-chip micro-supercapacitors

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<i>Keywords:</i> On-chip electronics Micro-supercapacitors MXene Potential window Energy density	On-chip micro-supercapacitors (MSCs) are one of the most promising devices to be integrated into micro-/nano- scale electronic devices for offering sufficient peak power and energy support. However, low operate voltage and limited energy density greatly inhibit their wider practical application. Herein, high-voltage on-chip MSCs based on $Ti_3C_2T_x$ MXene as a negative electrode and activated carbon as a positive electrode are designed and are simply manufactured via a novel cutting-spraying method. Through solving the excessive polarization of MXene, a single asymmetric on-chip MSCs can deliver a potential window up to 1.6 V in neutral electrolyte (PVA/ Na <sub>2</sub> SO <sub>4</sub> ), and share a high areal capacitance of 7.8 mF cm <sup>-2</sup> (a stack specific capacitance of 36.5 F cm <sup>-3</sup> ) and a greatly improved energy density of 3.5 mWh cm <sup>-3</sup> at a power density of 100 mW cm <sup>-3</sup> , which are much higher than other on-chip energy storage counterparts. Besides, MSCs show an excellent capacity retention (remaining 91.4% after 10 000 cycles). More importantly, MSCs can be easily enlarged as highly integrated array in series and/or in parallel on the silicon wafers. Evidently, this study opens up new avenues for developing high-voltage MXene-based MSCs used in on-chip electronics and portable devices.

## 1. Introduction

With the vigorously rising of internet of things (IoT) and the great improvement of the reliability of wireless communication protocols [1], lots of related sensors [2-5], and portable and wearable electronic devices [6-8], spring up to sense and interact physical worlds for the development of a smarter life. However, due to the intermittency of the renewable resources (wind [9], solar [10], tidal [11], and geothermal energy [12]), achieving the integration of on-chip energy-storage units with novel electronic devices is an essential step for stable power supply [13–15]. With high energy density [16], conventional micro-batteries are capable to keep the devices working for some period of time but the low power density and lack of the necessary cycle life make it impossible to meet the requirement of rapid power delivery in application where battery replacement may not be practical [17-19]. As an alternative to micro-batteries, micro-supercapacitors (MSCs) have drawn broad attention on account of the intriguing advantages of long lifetime, high power density and fast charging rate [20-26].

Nevertheless, the limited power and energy density are always holding back their further development in the field of microelectronics [27–30].

As a new type of two-dimensional material, MXenes share a uniquely layered structure combining highly electrical conductive layer and rapid ionic transport layer that make them ideal candidates to meet the requirement of state-of-the-art MSCs [20,31,32]. In recent years, MXene-based supercapacitors with extremely high volumetric performance [33], ultra-high-rate capability [34] and flexible AC-filtering ability [35,36] made MXenes' impressively promising application in capacitive energy storage. However, MXene-based on-chip MSCs are still in infancy and too low operated voltage window is still one of the major drawbacks [37]. For the later, once MXenes are subjected to a positive potential (like 0.2-0.4 V above the open circuit potential) in aqueous electrolyte, the excessive polarization would occur, leading to an increase in resistance and finally losing their efficacy during a relatively long-term duration [38]. In fact, MXenes were turned to be typically negative electrode materials as used to be supercapacitor electrode material [39], ascribing their pseudocapacitive mechanism that





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originates from dynamically adsorbing/desorbing protons to change the valence state of transition metals as well as oxygen functional groups [40–42]. Therefore, resorting to materials and cell design own its original interesting for building high-voltage MXene-based MSCs.

In light of the above-discussed issues, we firstly design and construct high-voltage asymmetric MXene-based on-chip micro-supercapacitors by pairing  $Ti_3C_2T_x$  as a negative electrode and activated carbons (ACs) as a positive electrode. These two types of electrode materials can well avoid the polarization of MXene undergone high positive potential. The simply cutting-spraying technology was employed to fabricate asymmetric MSCs with in-plane interdigital microelectrodes, and addressed well with the challenge of matching positive and negative electrodes. Owing to the synergistic effects among the electrode materials, the gel electrolyte (PVA/Na<sub>2</sub>SO<sub>4</sub>) and the asymmetric device structure, MXenebased on-chip MSCs can be operated at a high voltage window of 1.6 V, which is much higher than that of symmetric MXene-based MSCs. Such high potential window in combination with in-plane designed microelectrode architecture enable it realizing a maximum areal capacitance of 7.8 mF cm<sup>-2</sup> at 400  $\mu$ A cm<sup>-2</sup> and a stack capacitance of 36.5 F cm<sup>-3</sup> at  $2.01 \times 10^5 \ \mu A \ cm^{-3}$ . Accordingly, this high-voltage MXene-based onchip MSCs deliver a high energy density of  $3.5 \text{ mWh cm}^{-3}$  (at a power density of 100 mW cm<sup>-3</sup>), which is much superior than the other reported on-chip energy storage devices [43-45]. In addition, our MSCs show an excellent capacitance retention of ~91.4% after 10 000 cycles. Based on it, we developed the easily enlarged and highly integrated array in series or in parallel or both on the silicon wafers, revealing the excellent silicon-based integrateability and compatibility. Unambiguously, these positive results demonstrate that MXene-based on-chip MSCs with high operated voltage possess a greatly potential application in highly integrated electronics and portable devices as power supply, energy support or both.

#### 2. Results and discussion

The design and work principle of high-voltage on-chip MXene-based MSCs are shown in Fig. 1a. The high-voltage was realized through elaborately designing from three parts. Firstly, a positive electrode of ACs (YP50 type) was introduced to avoid the polarization phenomenon of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> at the positive potential. This is important for Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene since it is a typically negative material [46] that originates from the transition between different valence state of Ti atoms induced pesudo-capacitive mechanism [40,47,48]. As MXene experiences the duration of charging-discharging process, the Ti k-edge change in Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> induces the valence state variation of Ti atoms that determines typlical pseudocapacitive effect of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene [49]. However, the potential window of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene in Na<sub>2</sub>SO<sub>4</sub> electrolyte can only stable at a range of -0.6 to 0.3 V (Fig. 1b), a higher positive potential (like > 0.3 V)

will lead to raised CV curves that corresponds to the excessive polarization. After an asymmetric structural design by incorporating the positive activated carbons (ACs) electrodes can make the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene only work at the negative potential (-0.8 to 0 V). Secondly, a neutral gel electrolyte consisted of PVA and Na2SO4 was optimally selected to broaden the work voltage because it shares higher electrochemical stability than acidic, basic electrolytes as well as liquid electrolyte [46,50, 51]. Thirdly, the charge storage based on the areal capacitance between the positive and negative electrodes was elaborately optimized and balanced for eliminating the unacceptably excessive polarization within the potential window. The previous reported work had already demonstrated that the MXene materials versus graphite electrode could deliver much higher electrochemical properties comparing with Pt electrode through enlarging hydrogen evolution potential [52]. Under these synergistic actions of multiple strategies,  $Ti_3C_2T_x$  and AC based asymmetric on-chip MSCs can ultimately deliver a high voltage of 1.6 V, which is much higher than that of symmetric MXene-based MSCs (only 1.2 V). This greatly enhanced work potential would intrinsically result in high energy and power density simultaneously, which is very important for promoting the gradually miniaturized micro-electronics like integrated circuit (shown in Fig. 1a).

Further, to determine the stable potential window of MXene-based on-chip MSCs, a three-electrode was carried out with a Pt foil as a counter electrode and an Ag/AgCl electrode as a reference. As shown in Fig. 1b, the cyclic voltammetry (CV) curves of both MXene and AC electrode exhibit relatively rectangular shapes, but a slightly raised peak can be observed at around 0.1 V of MXene because the intercalation pseudocapacitance will naturally occur when ions intercalated/inserted into layered crystalline materials [53]. This process can be described by Eq. (1):

$$MA_{y} + zNa^{+} + e^{-} \leftrightarrow Na_{z}MA_{y} \tag{1}$$

where  $MA_y$  represents the layer-lattice intercalation electrode material and z is the transferred electrons number. Instead, an EDLC forms spontaneously at the electrode-electrolyte interfaces to physically store the charge. With the potential windows in the ranges from -0.6 to 0.3 V (vs Ag/AgCl) and 0-1.0 V (vs Ag/AgCl) of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene and ACs, onchip MSCs are capable to deliver a high voltage window of 1.6 V that is much higher than other MXene based MSCs [20,45,54,55].

As shown in Fig. 2, this high-voltage MXene-based on-chip MSCs was constructed through a simply cutting-spraying method, which can well solve the problem that the positive and negative electrodes cannot be attached to the substrate without mutual interference for charge balancing. The whole working area of the microelectrodes with an interdigitated pattern was defined using a simple and economical kapton tape as a mask, and the cold ultraviolet (UV) laser (355 nm) was used to engrave the pattern and cut the silicon wafer (Step I). Then, an Au/Cr



**Fig. 1.** Designing and constructing high-voltage on-chip MXene-based micro-supercapacitors (MSCs). (a) Schematically illustrating the internal structure and work principle of on-chip MSCs; (b) CV curves of MXene negative and activated carbon (AC) positive electrodes at a scan rate of 10 mV s<sup>-1</sup> in a three-electrode configuration, and the realization of high-voltage for on-chip MSCs are clarified based on analyzing the charge storage mechanism.



**Fig. 2.** The cutting-spraying manufacture process of high-voltage MXene-based on-chip MSCs on silicon wafer. The asymmetric on-chip MSCs based on  $Ti_3C_2T_x$  negative electrode and AC positive electrode were built through a simply cold laser-cutting and spraying method. And the whole device was encapsulated by a thin-layer polydimethylsiloxane (PDMS) through an improved mold-assisted forming method.

conductive layer was prepared by magnetron sputtering (Step II). The incorporation of Cr layer lies to its buffer effect during the Au/Cr alloy formation so that the Au layer can adhere well to the silicon wafer [56]. After that, the electrode materials were sprayed onto the Au microelectrodes selectively by a designed PET mask covered another electrode in advance (Steps III-IV). The Au layer as a current collector can avoid the accumulation of charge, which leads to excessive polarization of MXene due to the high potential. Thus, a MXene-based on-chip MSC with 6 in-plane interdigital microelectrodes was easily constructed. With the help of mask, another part was sprayed onto ACs films and the interdigital in-plane electrodes was obtained (Step V-VI). Finally,  $PVA/Na_2SO_4$  gel electrolyte coat was employed as the solid-state electrolyte and then polydimethysiloxane (PDMS) was utilized to encapsulate the whole device (Step VII-VIII).

Unlike conventional micro-fabrication methods, this 'cutting-spraying' method can not only avoid burning the edge of the microelectrodes, but also is suitably applied for large-scale and low-cost manufacturing. Moreover, in comparison with our previously reported 'treating-cuttingcoating method' [31], the treating process was replaced by establishing a buffer layer of Cr. This is a critically important improvement since the



**Fig. 3.** The microstructure and compositions of high-voltage MXene-based on-chip MSCs. (a) The photograph of the on-chip MSCs; (b) Raman spectra of the  $Ti_3C_2T_x$  MXene electrode coated on silicon wafer and the Raman spectra of  $Ti_3C_2T_x$  powder; (c) XRD patterns of MXene electrode coated on silicon wafer and the  $Ti_3C_2T_x$  powder; (d) SEM image showing the width of interdigital gap for on-chip MSCs; (e–f) Cross-sectional SEM images displaying the morphology and determining the thickness of both electrodes.

treating process commonly incorporation of strong acid and/or oxidizer will lead to destructing the surface structure of silicon wafer, which is very susceptible to silicon-based electronics. Notably, a mold-assisted forming method yielded a uniform encapsulation layer of PDMS (Fig. S1) solves the extinction problem of gel electrolyte, which is prerequisite to obtain the chemically stable MSCs.

This cutting-spraving method is highly simple and efficient to manufacture on-chip MSCs without causing any die edge damage and materials phase transition. Fig. 3a shows the digital photograph of a single on-chip MSCs. Raman spectroscopy was used to characterize various chemical and termination species of the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene (Fig. 3b). These Raman results clearly imply that MXene films had the same response as Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> powder, indicating the remained MXene structure after experiencing cutting-spraying processes. In addition, peak positions at around 242, 445 and 610 cm<sup>-1</sup> match well with the theoretically calculated values, indicative of  $Ti_3C_2T_x$  MXene [41,48]. Further, X-ray diffraction (XRD) was employed to confirm the crystal structure of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene. As shown in Fig. 3c and Fig. S2, the disappeared Ti<sub>3</sub>AlC<sub>2</sub> characteristic peaks within 36–45° clearly indicate the Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene film-electrode is successfully prepared. Comparing with  $Ti_3C_2T_r$  powders,  $Ti_3C_2T_r$  films coated on-chip show no apparent decline of interlayer spacing as indicated by their similar  $2\theta$  degree of (0 0 2) crystallographic plane, which will guarantee high capacitive performance.

Typical MXene-based on-chip MSCs share a gap of 260 µm between the adjacent interdigital microelectrodes and each microelectrode, which was 1.7 mm in width and 8.7 mm in length (Fig. 3d). SEM crosssectional images obviously presents two electrodes with the thickness of around 7.6 µm and 2.6 µm, respectively (Fig. 3e and f). Clearly, positive (ACs) and negative (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene) electrodes show a disordered porous and laminated morphology, respectively. And the laminated onchip Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> films confirms that accordion-like layered structure is well retained for Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> materials which was synthesized through a mild etch method using LiF and HCl solutions (Fig. S3). Importantly, the optimum thickness ratio of the positive to negative electrodes is about 3, which is agree with the calculated value in methods (**Note. 1** and **Table S2**). This optimally balanced charge storage strategy based on the areal capacitance between the AC positive and MXene negative electrodes would be helpful for high-voltage on-chip MSCs, just as shown in the following discussed electrochemical performance.

The electrochemical properties of a single on-chip MSCs were shown in Fig. 4. The CV curves at different scan rates illustrate a good capacitive-like profile for on-chip MSCs. Even at a high scan rate of 200  $mV s^{-1}$ , the capacitance is still well retained, indicating a rapid charge storage property. For comparing, symmetric MXene-based on-chip MSCs with the same MXene electrode thickness were also prepared. Their CV curves display a relative sharp polarization when the potential is close to 1.2 V at a scan rate of 10 mV  $s^{-1}$ , the positive electrode MXene has almost no performance due to its positive voltage, resulting in no obvious redox peak that can be observed and low specific capacitance (Fig. S4). Amazingly, the areal capacitance is nearly five times for asymmetric on-chip MSCs higher than symmetric on-chip MSCs (Fig. S5). Meanwhile, the GCD curves exhibit typical isosceles at 100 µA  $cm^{-2}$  (Fig. 4b). And the larger curve and the longer discharge time also indicate much larger areal capacitance asymmetric on-chip MSCs (7.8 mF cm<sup>-2</sup>) than symmetric one (1.8 mF cm<sup>-2</sup>).

Further, the electrochemical impedance spectroscopy (EIS) analysis (Fig. 4c) offers insights into the electrochemical capacitive behavior. It should be noted that a curve in the fourth quadrant, which is caused by inductance. The obtained data at the frequency ranging from  $10^{-2}$  to 10<sup>5</sup> Hz were further fitted by an equivalent circuit using Z-view software. And the equivalent circuit was shown in the inset of Fig. 4c, where  $R_0$  is the internal resistance,  $R_{ct}$  represents the charge-transfer resistance,  $W_0$  is the Warburg impedance, and CPE1 is double-layer capacitance. At high frequency range, both of the Nyqusit plots exhibit a semicircle but the asymmetric on-chip MSCs possess a lower  $R_0$  value. While in the low-frequency region, the Nyqusit plots share a straight long tail and near the vertical direction, indicating good capacitive behavior. The internal resistance of asymmetric MXene-based on-chip MSCs are smaller than the symmetric MXene-based on-chip MSCs, mainly due to the particle size of the sulfate ion in the symmetric MXenebased on-chip MSCs is relatively large and cannot be inserted into the MXene sheet. But in asymmetric MXene-based on-chip MSCs, the activated carbon of the positive electrode is porous, and sulfate ions can attach to the surface of the material to form an electric double layer.

Fig. 4d shows the corresponding GCD curves of asymmetric on-chip



**Fig. 4.** Electrochemical properties of a single high-voltage MXene-based on-chip MSCs. (a) CV curves at the scan rates varying from 5 to 200 mV s<sup>-1</sup>; (b) GCD curves comparison of the asymmetric on-chip MSCs and the symmetric on-chip MSCs at 100  $\mu$ A cm<sup>-2</sup>; (c) The Nyquist plots and the fitted equivalent circuit; (d) GCD curves at different current densities; (e) The calculated areal capacitances; (f) The Ragone plots of the device.

MSCs at various current densities from 200 to 2000  $\mu$ A cm<sup>-2</sup>. All the curves exhibit the isosceles triangular shape, indicating the fast kinetics. The areal specific capacitances of the high-voltage MXene-based on-chip MSCs at different current densities were calculated from GCD curves in Fig. 4e. With the current density increasing from 100 to 2000  $\mu$ A cm<sup>-2</sup>, the areal capacitance retention of 59% can be still obtained. As shown in Table S1, the specific capacitance of high-voltage MXene-based on-chip MSCs are higher than the other reported on-chip MSCs [57–60] and asymmetric MSCs [61,62]. The stack specific capacitance of the high-voltage MXene-based on-chip MSCs up to 36.5 F cm<sup>-3</sup> at 2.01  $\times$  10<sup>5</sup>  $\mu$ A cm<sup>-3</sup> (Fig. S6), and the stack capacitance retention of 70% can be still obtained with the current density increasing from 2.01  $\times$  10<sup>5</sup> to 4.02  $\times$  10<sup>6</sup>  $\mu$ A cm<sup>-3</sup>.

Since the work voltage was efficiently enhanced, the volumetric energy and power densities of high-voltage MXene-based on-chip MSCs were accordingly improved drastically as shown in Fig. 4f. These MSCs exhibited a high energy density of  $3.5 \text{ mWh cm}^{-3}$  at a power density of 100.6 mW cm<sup>-3</sup>. Even at a high power density of 2.01 W cm<sup>-3</sup>, a high energy density of  $1.73 \text{ mW} \text{ h cm}^{-3}$  was also realized, reaching the stateof-the-art MSCs metrics [63,64]. Amazingly, its volumetric energy density can be comparable to Li-ion thin-film batteries (10 mWh  $cm^{-3}$ ), while the corresponding power density has gone far beyond it. Also, the corresponding volumetric energy density was 3 orders of magnitude higher than commercial Al electrolytic capacitor and 1 order of magnitude higher than other microsupercapacitors [65]. And also much superior than other classes of electrode materials including laser-scribed graphene (~0.4 mWh cm<sup>-3</sup> at 560 mW cm<sup>-3</sup>) [66], commercial AC  $(\sim 0.7 \text{ mWh cm}^{-3} \text{ at 575 mW cm}^{-3})$ , and MXene-based symmetric on-chip MSCs ( $\sim$ 1.06 mWh cm<sup>-3</sup> at 387 mW cm<sup>-3</sup>) [31].

We further proved the large-scale integrateability of MXene-based on-chip MSCs (see Fig. 5). As shown in Fig. 5a, a digital photograph obviously presents three units in series and four units in parallel MSCs arrays on a whole silicon wafer with a diameter of 3.9 inches. The corresponding CV and GCD curves of the integrated MSCs in series or in parallel are shown in Fig. 5b–c. After integration, the working voltage of the on-chip MXene-based MSCs can be further improved from 1.6 V to 3.2 V verified by both CV and GCD tests. As expected, the stored charge of two MSCs in parallel was two times than the single one at the same CV

scan rate and GCD current density. Further, as shown in Fig. 5d, this integrated device can light a commercial LED lamp, sufficiently revealing the superior performance of high-voltage on-chip MXenebased MSCs. Meanwhile, these MSCs possessed a very long-term cycling lifetime of retaining 91.4% areal capacitance after 10 000 cycles, which is due to the fact that there is no substantial structural change in MXene when Na<sup>+</sup> is intercalated/deintercalated during the electrochemical reaction [49] (Fig. 5e). Besides, the greatly improved encapsulated technology was authentically critical for superior cycling stability. In fact, the traditional package technology of supercapacitors based on vacuum heat sealing was proved to be not appropriate for micro-supercapacitors. In this work, the improved encapsulation technology based on mold-casting of PDMS can efficiently avoid the heat-sealing and vacuum-treatment process, which usually suffer from the bubble-expanding induced instability of gel solid-state PVA/Na<sub>2</sub>SO<sub>4</sub> electrolyte layer and PDMS encapsulation layer. Therefore, this mold-casting technology can uniformly form an encapsulated layer and efficiently avoid the further dehydration-induced solidification of gel electrolyte. Finally, the cycling stability determines purely from the electrode materials of MXene and ACs, two kinds of well-known materials with very high electrochemical stability.

## 3. Conclusion

In summary, we developed one kind of high-voltage asymmetric MXene-based on-chip micro-supercapacitors (MSCs). The asymmetric structure well avoided the excessive polarization of  $Ti_3C_2T_x$  MXene undergone high positive voltage, these high-voltage asymmetric MSCs realized a high potential window of 1.6 V in neutral electrolyte (PVA/Na<sub>2</sub>SO<sub>4</sub>), which is much higher than the previously reported symmetric on-chip MXene-based MSCs. In combination with designing an in-plane interdigital micro-electrodes with improved transmission of electrolyte ions, the high-voltage MXene-based on-chip MSCs could deliver simultaneously high energy density (3.5 mWh cm<sup>-3</sup>) and power density (100 mW cm<sup>-3</sup>). And these MSCs share an excellent cycling stability because of eliminating the encapsulation issue by incorporating a greatly improved mold-casting encapsulated technology. More importantly, high-voltage MXene-based on-chip MSCs can be further integrated into



**Fig. 5.** Arraying the single high-voltage on-chip MXene-based MSCs. (a) Digital photograph of three MSCS in series and four in parallel on silicon wafers with a diameter of 3.9 inches; (b) CV curves at 20 mV s<sup>-1</sup>; (c) GCD curves of single, two-series, and two-parallel devices at 400  $\mu$ A cm<sup>-2</sup>; (d) The on-chip MSCs in two-series can light a commercial LED lamp; (e) Cycling stability at 400  $\mu$ A cm<sup>-2</sup> (inset: the CV curves in different cycle number).

large-scale micro-energy storage devices by cutting-spraying manufacture technology with the advantages of large-scale, low-cost and simplyprocessed. These positive results clearly demonstrate the greatly potential applications of MXene-based on-chip MSCs in micro-electronics and potable electronics.

#### 4. Experimental section

**Preparation of**  $Ti_3C_2T_x$  **negative electrode material:** Multilayer  $Ti_3C_2T_x$  powder was firstly synthesized via etching MAX phase of  $Ti_3AlC_2$  (400 mesh, 11 Technology Co. Ltd) similar to our previous report [67,68]. Specifically, 1.98g of LiF was added into 30 mL of 6 M HCl and stirred for 10 min, followed by the slow addition of 1.2 g of  $Ti_3AlC_2$ . After etching for 45 h at 40 °C, the multilayer  $Ti_3C_2T_x$  was washed with deionized (DI) water and centrifuged until the pH value of supernatant reached 6.  $Ti_3C_2T_x$  powder was then dispersed in DI water and sonicated for 1 h. After centrifugation for 1 h at 3500 rpm, the few-layer  $Ti_3C_2T_x$  colloidal suspension was prepared.

**Preparation of ACs positive electrode material:** ACs positive electrode materials were made into slurry by mixing 85 wt% AC (YP–50F, BET: 1769 m<sup>2</sup> g<sup>-1</sup>), 10 wt% conductive agents (Super C45, Timcal), and 5 wt% binder (1 wt% carboxymethylcellulose + 4 wt% styrene-butadiene rubber) in planetary ball mill at 300 rpm for 2 h.

Constructing high-voltage MXene-based on-chip MSCs: Highvoltage MXene-based on-chip MSCs were produced by a simple cutting-spraying method. Briefly, kapton tape was stuck to the silicon wafer and then the interdigitated pattern was cut by an ultraviolet laser (UV-3S, China) with a constant power of 5 W, a cutting speed of 500  $\mathrm{mm}\,\mathrm{s}^{-1}$ , and the cutting time of 30 s. Notably, silicon wafer has a 300 nm thick SiO2 oxide layer to avoid short circuit of the electrodes. Afterwards, the current collector was prepared by sputtering gold on silicon wafer for 5 min and using Cr as an adhesion layer. The silicon wafer with gold foil current collector was soaked in a sodium salt (HS-(CH<sub>2</sub>)<sub>3</sub>-SO<sub>3</sub>Na) ethanol solution for 30 min forming a monolayer of hydrophilic molecules, which can solve the problem of adhesion between electrode materials and current collector. The spraying step was followed with nitrogen under pressure of 0.2 MPa, when spraying one microelectrode, the other microelectrode was covered with PET paper as mask. Then, the interdigital microelectrodes were coated with a layer of PVA/Na<sub>2</sub>SO<sub>4</sub> and further stand for 30 min to make the gel electrolyte be a semi-solid state. Finally, polydimethylsiloxane (PDMS) module glue was used to completely package the device. The similar method was used to fabricate MXene based symmetric on-chip MSCs excepting that no implemented positive electrode was prepared.

**Characterizations:** Raman spectra were recorded using a HORIBA Jobin-Yvon XploRA ONE contocal Raman microscope with 532 nm laser and an air-cooled CCD dector. XRD patterns were collected on an X-ray diffractometer (PANalytical Empyrean, Holland) using Cu Ka radiation in the range of  $2\theta = 5-50^{\circ}$ . The morphologies of both the electrode materials and the devices were investigated by means of field emission scanning electron microscopy (FEI QUANTA FEG 250, American).

*Electrochemical measurements*: The electrochemical performance including CV, GCD, and EIS measurements were carried on an electrochemical workstation (CHI660E, China). Electrochemical cycling stability were conducted using a multi-channel galvanostat/potentiostat instrument (Arbin, USA) at room temperature.

*Calculation*: Mass ratio of positive and negative is calculated by the following equation.

$$\frac{m_{+}}{m_{-}} = \frac{C_{electrode-} \times \Delta E_{-}}{C_{electrode+} \times \Delta E_{+}}$$
(2)

And the areal capacitance (*C*), the energy density (*E*), and the power density (*P*) were determined as following.

$$C = \frac{\int IdV}{Av\Delta V}$$
(3)

$$\mathbf{E} = \int_{t_1}^{t_2} I V_t dt \tag{4}$$

$$P = \frac{3600E}{\Delta t}$$
(5)

where  $C_{electrode}$  is the mass specific capacitance (F g<sup>-1</sup>),  $\Delta E$  is the potential window of each electrode (V). *I* is the discharge current (mA), *A* is geometrical area of the device (cm<sup>-2</sup>), *v* is the scan rate (V s<sup>-1</sup>), and  $\Delta V$  is the operating discharge potential range (V),  $t_1$  is the time after the initial IR drop (s),  $t_2$  is the moment discharge end (s), and  $\Delta t$  is the discharge time (s).

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

Yanting Xie: Conceptualization, Writing - original draft. Haitao Zhang: Funding acquisition, Writing - review & editing, Conceptualization, Project administration. Haichao Huang: Investigation, Methodology. Zixing Wang: Investigation, Visualization. Zhong Xu: Validation. Haibo Zhao: Resources. Yuchen Wang: Resources. Ningjun Chen: Validation. Weiqing Yang: Funding acquisition, Writing review & editing, Project administration.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nanoen.2020.104928.

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