Fiber-shaped Fluidic Nanogenerator with High Power Density for Self-Powered Integrated Electronics

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Summary

Flow-based hydrovoltaic nanogenerators have attracted particular attention as efficient and facile miniature energy harvesting. However, these devices deliver relatively low output power density and limited power conversion efficiency owing to inefficient charge separation and poor charge accumulation. Here, we report the fabrication of high-performance, fiber-shaped fluidic nanogenerators (FFNGs) that employ MoS_2-encapsulated carbon fibers. The FFNGs deliver stable output voltages of 540 mV and ultrahigh power density of 10.8 W m^{-2}. With experiments and density functional theory calculations, improvements in output performance can be attributed to smaller energy requirements for Na^+ cation adsorption, increased charge separation, and diffusion layer formations on the near surface. Moreover, self-powered, integrated devices achieve a maximum total power conversion-storage efficiency of ~11% and stable output voltage up to 3.1 V, which is applicable for use in consumer electronic devices.

Keywords: Carbon fiber; MoS_2 nanosheets; Hydrovoltaic nanogenerators; High power density; Self-powered; Integrated electronics

Introduction

Energy harvesters that can efficiently convert energy from natural phenomena, such as sunlight, water and wind, into high power output applications are urgently needed to realize a sustainable society.[1,2] Different harvester types include photovoltaic,[3,4] thermoelectric,[5] hydrovoltaic[6,7] and triboelectric devices.[8,9] Hydrovoltaic devices in particular can provide continuous, stable power generation as they are not influenced by the time of day or weather. Some hydrovoltaic harvesters are already in use harnessing mechanical energy from water flow in dams.[10] However, harvesting mechanical energy from flowing water requires complicated, large scale facilities and significant height differences, which may be difficult to replicate in minitype self-powered systems.[11,12] To address this challenge, researchers have devoted much efforts into the fabrication of hydrovoltaic devices that utilize

interactions between liquid flow/droplets/moisture and nanomaterials. A variety of methods based on different mechanisms, including electrokinetic, alternating potential, and ionization effects, have been explored. In 2003, researchers reported that pumping HCl solution through single-walled carbon nanotubes (CNTs) induced electric current and voltage based on the movement of the free charge carriers.[13] Subsequently, many nanomaterials with different surface properties, such as graphene,[14-16] CNTs,[10,17,18] and polymers,[19,20] have been utilized. For instance, a layered graphene hydrogel membrane showed a total ionic current of 2200 pA and 5.1 nW of power when electrolyte flowed in the vertical direction, which is attributed to the electrokinetic phenomenon.[21] Porous carbon films generate a power density of 30 nW cm^{-2} from water evaporation and proton movement guided by the oxygen concentration.[22] TiO_2 nanowires[11] and polypyrrole (PPy) skeletons[20] can achieve power densities of 25 μW cm^{-2} and 10 nW cm^{-2}, respectively, due to proton gradient distributions. In addition, oxygen-treated CNT yarns can discharge electricity with a power density that exceeds 0.07 mW cm^{-2} due to polarization-induced dissociation effects.[18] Nevertheless, electricity generated from hydrovoltaic effects show low output power density (more details in Table S1) and limited power conversion efficiency. This may be due to weak interfacial interactions that exist between material surfaces and ions in solution, especially inefficient surface charge separation.[6,23] Consequently, power density of hydrovoltaic devices are far from satisfactory and must be improved to the meet demands of practical applications.

Although the mechanisms proposed to date still have not been verified, key factors for maximizing hydrovoltaic device performance include strength of the interfacial interaction and transport rate of charges in materials. These factors can be optimized by adjusting surface properties and resistance of materials, respectively[6,23]. Here, we fabricate fiber-shaped fluidic nanogenerators (FFNGs) capable of high power output with MoS_2-functionalized carbon fibers (MSCFs) that can simultaneously promote charge interaction with ions in aqueous solution and decrease the resistance of composite materials. The FFNGs exhibit a stable, high voltage output of 540 mV,

an ultrahigh power density of 10.8 W m^{-2}, a maximum power conversion efficiency of 21.4%, and outstanding stability without obvious back-relaxation even after 1000 cycles. More importantly, experimental tests coupled with density functional theory simulations show that MoS_2 with a lower zeta potential has more negative charges on the surface, which provides lower adsorption energies for Na^+ cations. This phenomenon promotes efficient charge separation and provides net charge accumulation that leads to the formation of a diffusion layer on the surface. This greatly enhances charge separation and potential/current output in hydrovoltaic nanogenerators. Moreover, self-powered integrated devices consisting of an energy harvester, an energy storage device, and a strain sensor are assembled for the first time. These devices achieve a total power conversion-storage efficiency of 10.54%, stable output voltage. To the best of our knowledge, both the output power density and power conversion efficiency are among the best for reported fiber-shaped devices. The self-powered system with the FFNG energy harvester can supply an output voltage of 3.1 V to power a green light-emitting diode (LED) and a commercial digital timer, which demonstrates potential for application in minitype self-powered energy devices.

Results and Discussion

FFNG Setup and Material Characterization

The experimental configuration for the setup of FFNG device is illustrated in Figure S1 and 1A, where a bundle of MSCF with a diameter of 1.0 mm was twined by conductive Cu wire, and the interface between the MSCFs and Cu wire was protected with waterproof adhesives to avoid contact with the aqueous solution. Then the MSCFs were placed in the centre of transparent plastic pipe and both ends were sealed with hot-melt adhesives. To measure the electricity generation in the FFNGs based on MSCFs, a commonly found NaCl aqueous solution, similar to seawater or biological fluid, served as the mobile phase flowing through the tube and contact fibers to systematically study the electricity generation of the FFNGs. The MSCFs were prepared using a scalable hydrothermal process (see experimental section for details)

that could continuously prepare MSCFs and wrap them in a roll (Figure 1B). Compared to the relatively smooth surfaces of carbon fibers (Figure S2A), MSCF surfaces showed a large number of carbon fibers covered by flower-like nanosheets (Figure S2B and 1C), which suggested the formation of MoS_2 nanosheets. Cross-sectional SEM images of the MSCFs verified that MoS_2 nanosheets with approximately 190 nm heights were distributed in vertical arrays across the surface (Figure 1D). Additionally, elemental distribution mappings of S and Mo obtained using energy dispersive spectroscopy (EDS) indicated uniform distribution of MoS_2 on the surface (Figure S3). High-resolution transmission electron microscopy (HRTEM) images revealed that the well-resolved lattice fringes had an interlayer distance of approximately 0.65 nm (Figure S4A and B), which corresponded to the (002) plane of 2H-MoS_2. This was found to be consistent with selected area electron diffraction (SAED) pattern (Figure S4C) results.[24] All the peaks of the X-ray diffraction (XRD) pattern shown in Figure 1E are ascribed to 2H-MoS_2 (JCPDS No. 73-1508), except for the obvious peak at approximately 25.5°, which was attributed to the (002) plane of carbon fibers and implied a highly crystalline phase. X-ray photoelectron spectroscopy (XPS) analysis clearly showed the emergence of a Mo peak located at approximately 229.7 eV and a S peak located at 162.0 eV after the hydrothermal reaction (Figure 1F and S5). The atom ratio of S:Mo obtained from the XPS element analysis is approximately 2:1 (Table S2), confirming the chemical composition of MoS_2. [25,26] In Figure S5A, high-resolution XPS spectra of S2p shows two valence states of S ($2p_{1/2}$ and $2p_{3/2}$), corresponding to MoS_2. Furthermore, the high-resolution XPS spectra of Mo 3d can be deconvoluted into two sets of peaks, which can be assigned to intrinsic MoS_2 (i-MoS_2, 232.5 and 229.4 eV) and defective MoS_2 (d-MoS_2, 232.9 and 229.7 eV) (Figure S5B). This revealed the existence of defects in the MoS_2 nanosheets.[27] Ultimately, the strong S 2s peak at 226.7 eV indicated the existence of S vacancies in the defective MoS_2 nanosheets,[28,29] which might have increased surface electron density and enhanced interaction with the solution ions, thus promoting efficient charge separation.

Electricity Generation Performance of FFNG

To evaluate electric signal generation, the FFNGs were operated with flowing NaCl aqueous solution. Current output linearly increased with applied voltage in the FFNG, whether operation occurred a dry state or in a 0.6 mol L^{-1} NaCl solution. This illustrated good ohmic contact and a low resistance of approximately 12.0 Ω cm^{-1} (Figure S6). Interestingly, a stable voltage output (V_{op}) of 540 mV and a current output (I_{op}) of 2.0 mA was obtained from the 5-cm-long MSCF-based FFNGs (Figure 2A and S7), which showed outstanding current output and high voltage. At the same time, while reversing the flow direction of NaCl solution, a V_{op} of -413 mV and an I_{op} of -0.12 mA can also be obtained (Figure S8). However, the V_{op} of MoS_2-free carbon fibers in the flowing 0.6 mol L^{-1} NaCl solution was approximately 2.5 mV (Figure S9), which indicated that the outstanding voltage induced by the MSCFs was mainly attributed to the MoS_2 nanosheets. Additionally, the MSCF-based FFNGs exhibited steady current and voltage output over 300 s. Different configurations of the FFNGs were compared to better understand performance factors (Figure S10). Regardless of whether the ends of the FFNGs were both immersed in the NaCl solution or both exposed, only a negligible output voltage could be observed. This suggested that electricity generation in these devices was based on a flow-induced mechanism rather than classical electrokinetic theory or the droplet-drawing potential.

To gain further insight into FFNG operation, electricity generation performances were studied as a function of NaCl concentration and flow velocity. As expected, V_{op} increased with increasing NaCl concentration, which suggests that induced voltage is dependent on solution concentration (Figure 2B). By increasing NaCl solution concentration from 0 to 0.6 mol L^{-1}, the V_{op} increased from 0 V to 520 mV. Then, V_{op} slowly increased even as concentrations increased above 0.6 mol L^{-1}, and increased up to 540 mV at a concentration of 4.0 mol L^{-1}. Furthermore, it was discovered that the V_{op} output was directly influenced by the flow velocity of the salt water solution (Figure 2C). The V_{op} increased from 50 to 520 mV as flow velocity was increased from 1.2 to 78 cm s^{-1}. This reached a maximal value of 540 mV at a flow velocity of 90 cm

s^{-1}. We also investigated the V_{op} with increasing the effective length of the MSCF. It can be found that the V_{op} is increased from 342 to 667 mV with the length increasing from 1 to 10 cm. But a V_{op} of 452 mV was obtained as the length is increased to 15 cm, which may be attributed to the increase of inefficient utilization in long flow distance in the solution (Figure S11). Moreover, the V_{op} and I_{op} of the 5-cm-long FFNG in a 0.6 mol L^{-1} NaCl solution was investigated by connecting the device to an external load (Figure 2D and E). With increasing external resistance, the induced voltage and current reached maximum values of 540 mV and 2.0 mA at a load resistance of 0.4 MΩ, which provided a maximum power density of 10.8 W m^{-2} (Figure 2E). This maximum power density and output current are among the highest values for previously reported water-based electric generation devices, regardless if device operation is in humid environments,[11,15,19,30-32] flowing water[18] or ionic aqueous solutions[10,14] (Figure 2F and Table S1). In addition, based on the above electricity generation properties, the power conversion efficiency, namely, the ratio of the electric output energy of the FFNG to the mechanical input energy of the salt water, was calculated according to the following equation: $\eta = 2UIt/\rho V v^2$. Here U represents the V_{op} and I represents the I_{op} of the FFNG during the flow process, v represents the flow velocity of salt water, and ρ and V represent the density of the NaCl solution and the volume of the NaCl solution within the flow time (t), respectively. As shown in Figure 2C and S7, a maximum power conversion efficiency of ~21.4% can be achieved in a 0.6 mol L^{-1} NaCl solution at a flow velocity of 16 cm s^{-1}. MSCF morphologies were maintained without obvious changes throughout testing even after 1000 cycles of electricity generation (Figure S12). In addition, XRD patterns and XPS spectra after a 1000 cycle test were well consistent with those taken before device operation (Figure S13), which revealed excellent structural stability. More importantly, the FFNG device achieved outstanding long-term repeatability without noticeable output voltage decay over 1000 cycles (Figure 2G).

Flexible energy devices have recently attracted extensive attention due to their promising application in miniature/portable electronics.[33,34] Electricity generation of a

10-cm-long woven FFNG device moving vertically in a 0.6 mol L^{-1} NaCl aqueous solution was investigated (Figure 3A and B) to understand the intrinsic mechanisms between MSCFs and ionic aqueous solutions. As shown in Figure 3C and D, a typical V_{oc} of 40 mV and an I_{sc} of approximately 2 mA was generated by the MSCF-based woven FFNG device at a moving speed of 5 cm s^{-1}. The voltage output was highly stable and showed no obvious decrease over 50 cycles. Moreover, the influence of different moving speeds on the voltage output of the woven FFNG was also investigated (Figure 3E). Impressively, the woven FFNG device exhibited an obviously increased V_{oc} when velocity was increased from 2.5 to 12 cm s^{-1} and provided high voltage outputs of approximately 20, 40, 60, 120 and 150 mV at moving speeds of 2.5, 5.0, 8.0, 10.0 and 12.0 cm s^{-1}, respectively. Such a trend seems to suggest that electricity generation is dependent on moving velocity. In repeated tests at different velocities, the woven FFNG device provided stable voltage output, showed good stability, and repeatability. These results demonstrate that electricity can be generated from the relative motion between MSCFs and an ionic solution. The voltage output highly depends on the relative velocity and the interaction of fiber and ions in the solution. Compared with the fiber placed in the plastic pipe in Figure 2, the structure of woven textile of the MSCF and cotton yarns is different. The hybrid textile with the inactive cotton may lower the relative speed on the fibers and effective contact area, so the corresponding output voltage is lower to some extent.

Mechanism Analysis of Electricity Generation

According to the above results, electricity generated in the MSCF-based FFNG devices clearly arose from the flow of ions along the MSCF surfaces. Potential differences can emerge and be measured on the electrodes with the movement of certain NaCl solution concentrations or the MSCFs themselves. However, the hydrovoltaic voltage can only be generated when only one end of the MSCF-based FFNG device is in contact with the liquid solution. When both ends of the MSCF-based FFNG device were in contact with the salt solution or exposed, only several microvolt output was detected. Inspired by previously reported work,[6,10,23] a possible mechanism based on electric double layer

(EDL) separation was proposed, as illustrated in Figure 4A. Specifically, when the NaCl aqueous solution contacts the MSCFs, Na^+ ions with positive charges are adsorbed on the negatively charged surface of the MoS_2 with a zeta potential of -45 mV (Figure 4B), forming a Stern layer.[35] In a steady state, a dynamic equilibrium between Na^+ and Cl^- can be achieved on the whole solid-liquid interface. When the NaCl solution flows on the MSCF surface, the Cl^- migration in the diffusion layer is retarded at the front end of the NaCl solution and cannot counteract the positive charge of Na^+ ions in the Stern layer, causing an uneven distribution of positive charge along the fiber. This draws electrons from the fiber surface to balance the net charge, thereby leading to an accumulation of net charges and generation of a potential difference.[10,23] This induced voltage has been reported to be proportional to the conductivity of the diffusion layer (counter ion number), which has a positive correlation with surface potential.[35,36] Correspondingly, the surface zeta potentials (ζ) of MoS_2 and carbon fibers in deionized (DI) water and 0.6 and 4.0 mol L^{-1} NaCl aqueous solutions were investigated, as shown in Figure 4B. In DI water, the zeta potential of MoS_2 nanosheets was approximately -45 mV, which is much lower than that of carbon fibers (-12 mV), indicating more negative charges on the MoS_2 surface. The more negative charges on the MoS_2 nanosheets can adsorb more Na^+ ions and spread more Cl^- ions in the diffusion layer to achieve charge balance, leading to a higher conductivity of the diffusion layer and an increased output voltage. Interestingly, compared to that of carbon fibers, the zeta potential of MoS_2 greatly increases with increasing NaCl concentration, thereby accounting for the improved output voltage. According to EDL diffusion theory, increasing salt concentrations observes an increase in zeta potential, which may be attributed to counter ion insertion into the Stern layer, the decreased thickness of the EDL and the enhanced conductivity of the diffusion layer, causing the increased output voltage. These results are consistent with the experimental results as shown in Figure 2B.[35,37,38] Additionally, the FFNGs have low resistance, as shown in the aforementioned results. Moreover, the FFNG devices consist of thousands of parallel carbon fibers, which leads to efficient charge transport in parallel circuits and

outstanding output current. Therefore, the FFNGs show increased power density due to the increased operation voltage and large output current.

The adsorption energies of Na^+ and Cl^- ions on the surfaces of MoS_2 nanosheets and carbon fibers were evaluated using density functional theory (DFT) calculations (Figure 4C-F, S14-16, see Supporting Information for the parameters used for the calculation).[39-42] DFT calculations showed that Na^+ ions could easily adsorb onto the (002) plane of MoS_2, as it only required an adsorption energy of -1.23 eV (Figure 4c and S15). However, Cl^- ions were repulsed by the surface of MoS_2, which resulted in an adsorption energy of 4.92 eV (Figure 4D and S15). In contrast, the adsorption energies of Na^+ and Cl^- on the surface of microcrystal carbon are 0.115 eV and -4.35 eV, respectively (Figure 4E, F and S16). These calculations clearly indicate that Na^+ ions are adsorbed more easily on the surface of MoS_2 compared to that of carbon. It has been reported that large amounts of surface ion adsorption can provide high EDL capacitance and induce large potential differences.[10] Therefore, cyclic voltammetry was used to reveal the EDL capacitance characteristics of the MSCF surface in different concentration salt solutions and a three-electrode system. No obvious redox peaks could be discerned, which indicated typical EDL behaviour (Figure S17). At the same time, the rectangular shape of the CV curve area increased with increasing Na^+ concentrations (Figure S17A), which represented higher levels of ion adsorption and EDL capacitance. In contrast, the semi-rectangular CV curve areas of carbon fibers in different concentration NaCl solutions are much smaller than those of the MSCFs. This suggest that much stronger EDL capacitive characteristics exist at the NaCl solution/MSCF interfaces (Figure S17B and C).

Self-powered Integrated Device and Application

To further demonstrate the potential application of FFNGs as efficient energy harvesters, a self-powered, integrated device consisting of an energy harvester (MSCF-based FFNG), an energy storage device (supercapacitors), and a functional device (flexible strain sensor) was fabricated, as shown in Figure 5A and S18 (see Supporting Information for the experimental details). The 5-cm-long MSCF-based FFNGs could

quickly charge supercapacitors to 0.5 V and provide a stable voltage bias for the strain sensor (Figure 5B and C). As shown in Figure 5B, the supercapacitors could be efficiently charged to 0.5 V in 90 s by the FFNGs and galvanostatically discharged at different discharge currents ranging from 50 to 200 μA. Interestingly, no obvious IR drop is observed at a high discharge current of 200 μA, which indicates excellent electrochemical performance. Furthermore, the total power conversion-storage efficiency can be calculated from equation of $\eta_{total} = 2W_{\mathrm{d}}/\rho V v^2$, W_{d} represents the discharge work of the supercapacitor, and V represents the volume of NaCl solution that flows out of the plastic tube during the charge process. Correspondingly, the total power conversion-storage efficiency of the self-powered integrated devices were 10.53%, 10.41%, and 10.32% at different galvanostatic-discharge currents (Table S3). This total efficiency exceeds that of previously reported, fiber-shaped, energy harvesting-storage, integrated devices,[2,4,43,44] and is comparable to the highest conversion-storage efficiency in two-dimensional self-powered integrated devices.[45-47] Additionally, the integrated device could be reversibly charged-discharged for 500 cycles and exhibited excellent cycling stability (Figure S19).

The outstanding properties of the self-powered integrated device enable it to work as a power supply for continuous strain sensor tests. As shown in Figure 5C, the strain sensor could respond to finger movements over a large range and demonstrated distinct current changes in repeated finger bending-stretching tests with the support of the integrated device. By integrating the device with a commercial management function, the self-powered integrated device could stably deliver an output voltage of 3.1 V (Figure 5D-G and Video 1), which meets the voltage requirements of traditional electronics devices and demonstrates good voltage adaptability.

In summary, high-performance, fiber-like, fluidic nanogenerators based on MSCF electrodes have been fabricated to harvest mechanical energy from flowing water or electrode shifts. These generators ultimately provide an output power density of 10.8 W m^{-2}, exhibit excellent stability, and realize a maximum total power conversion-

storage efficiency of 10.54% in self-powered integrated electronics. Further experimental tests and theoretical studies revealed that high voltage/current outputs may be attributed to efficient surface charge separation in the fibers and increased EDL capacitance, which arises from a smaller zeta potential and lower surface adsorption energy for Na^+ ions. This self-powered system, based on FFNG energy harvesters, exhibited stable power outputs of 3.1 V to various devise and holds promise for use in minitype energy devices.

Experimental Procedures

Resource Availability

Lead Contact

The lead contact for this paper is Bin Wang (binwang@caep.cn).

Materials Availability

This study did not generate new unique reagents.

Data and Code Availability

All data associated with the study are included in the paper and the Supplemental Information. Additional information is available from the Lead Contact upon reasonable request.

Chemicals

We purchased acetone (99%), ethanol (99%), H_2SO_4 (98%), $K_2S_2O_8$ (99%) $(NH_4)_6Mo_7O_{24}$•$7H_2O$ (99.7%) and thiourea (99.7%) from Chengdu Kelong reagent Ltd. Co. The carbon fiber with a diameter of 7 μm is purchased from Xianfeng carbon material Ltd. Co. All the reagents and solvents were directly used without further purification. And the deionized water was prepared with ultrapure water equipment (ULUP-I, Sichuan ULUPURE Ltd. Co.).

Preparation of MoS_2 encapsulated carbon fiber (MSCF)

0.529 g of $(NH_4)_6Mo_7O_{24}$•$7H_2O$ and 0.456 g of thiourea were dissolved in 25 mL of DI water to form a homogeneous solution. This mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave and the 50 cm long (0.15 g) pre-treated CFs were

placed in the solution (see supplemental experimental procedures for details of pre-treated process). The autoclave was then put into a 200 ℃ electric oven to promote hydrothermal synthesis reactions. After the hydrothermal reactions had completed, the samples were collected and washed several times with DI water. Samples were then annealed at 400 ℃ for 1 hour in argon atmosphere to obtain MSCF.

Materials Characterization

Morphology and elemental distribution were determined using a field-emission SEM equipped with an energy-dispersive spectrometer (Hitachi S-48000, Japan). TEM images were obtained with a JEM-2100F transmittance electron microscopy that operated at 200 kV. Photographs were taken with a digital camera (Nikon, J1). XRD patterns were characterized using X-ray diffraction (XRD, D/Max-2400) with Cu Kα radiation (λ = 1.5418 Å). XPS spectra were recorded with monochromatized Al Ka radiation (1486.6 eV) and fitted using XPS peak 4.1 software. Raman spectrum was determined using a HORIBA Jobin Yvon Evolution Raman spectrometer at room temperature with a 532 nm He-Ne Laser line. *I-V* and CV curves were carried out on a VSP-300 (Bio-Logic SAS, France) electrochemical workstation. Zeta potentials were measured with a dynamic light scattering particle size analyzer (DLS, Zetasizer Nano ZS90, UK).

Measurement of FFNGs and integrated device

To determine the electricity generation of the FFNG, one end of a bundle of MSCF with a diameter of 1.0 mm was directly twined with Cu wire. And the interface between the MSCFs and Cu wire was protected with waterproof adhesives to avoid contact with the aqueous solution. Then the MSCFs were placed in the centre of transparent plastic tube (2.0 mm in diameter) for fluid flow and both ends were sealed with hot-melt adhesive (as illustrated in Figure S1). NaCl solution was injected into the tube at different velocities from one end by a programmable peristaltic pump (Lead Fluid, BTS300-YT25). The other end was prevented from contacting the solution. For the vertical motion test, three pieces of cotton yarn and 10-cm-long MSCF were woven into one fiber. Two ends of this fiber were also connected with copper wires. One end

was tied with a heavy object. A FFNG was half-submerged in the NaCl solution and then moved up and down at different speeds. The output voltage and current between two ends were recorded at a VSP-300 (Bio-Logic SAS, France) electrochemical workstation.

Power conversion efficiency

Power conversion efficiency was defined as the ratio of FFNG electrical energy output to the mechanical input energy of the NaCl aqueous solution. FFNG electricity generation depends on the relative movement of solution or MSCF. For a FFNG based on MSCF that was placed into a plastic tube, electricity generation was originated from the movement of the aqueous solution in the lengthwise direction. So, the power conversion efficiency was calculated using the equation: $\eta = 2UIt/\rho V v^2$, where U and I represent the electric voltage and current output during the flow process, v represents the flow velocity, V represents the volume of NaCl aqueous solution in a certain time, and ρ is the density of 0.6 M NaCl solution (about 1.13 g cm^{-3}). Volumetric flow of the NaCl solution was calculated using the equation: $V = \pi(R^2 - r^2)vt$, where R and r are the radii of the tube (0.2 cm) and MSCF (0.1 cm), respectively, and t is the flowing time.

The total power conversion-storage efficiency of the integrated device was defined as the ratio of supercapacitor electrical energy output to the mechanical input energy of the NaCl solution, which was calculated by the equation: $\eta_{total} = 2W_{\mathrm{d}}/\rho V v^2$, where W_{d} represents the supercapacitor's discharge work and V represents the volumetric flow of NaCl solution from the plastic pipe during the charge process. Total electric output energy of the supercapacitor was calculated by the equation: $W_{\mathrm{d}} = \frac{1}{2}\int_{t_0}^{t_1} U_{\mathrm{d}} I_{\mathrm{d}} dt$, where $t_0 = 0$, t_1 is the discharge time, and U_{d} and I_{d} represent the discharge voltage and current, respectively.

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Author Contributions

J. Yang, J.L. Cheng, B. Wang and J. Lu designed research; J. Yang performed research; C. Yang, K.K., Guo and D.W. Yuan carried out the theoretical calculation; J. Yang, J.L. Cheng, B. Wang analysed experimental data; J. Yang., J.L. Cheng, B. Wang and J. Lu wrote the paper; and A. Dai, T.C. Liu, Y.F. Yuan discussed and edited the paper.

Declaration of Interests

The authors declare the patent (ZL201811313738.8, CN) related to this work.

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Figure Legends

Figure 1. FFNG setup and characterization of MSCF.

(A) Schematic of the setup used to measure FFNG electricity under flowing 0.6 mol L^{-1} NaCl aqueous solution.

(B) Photograph of prepared FFNG based on MSCFs, in a roll.

(C) SEM and (D) cross-sectional SEM images of the MSCFs at different magnifications. The inset is a cross-sectional SEM image of one fiber.

(E) XRD patterns of carbon fibers, MoS_2 powder, and MSCFs.

(F) XPS survey spectra of carbon fibers and MSCFs.

Figure 2. Electricity generation performance of FFNG.

(A) Voltage profiles for 5-cm-long FFNG submitted to 16 cm s^{-1} flow of 0.6 mol L^{-1} NaCl aqueous solution. The maximum voltage of the device reaches approximately 521 mV.

(B) Voltage dependence on the concentration of the NaCl aqueous solution. The error bars represent the mean absolute error from three samples at each concentration.

(C) Voltage dependence on flow velocity of 0.6 mol L^{-1} NaCl aqueous solution. Dependence of (D) voltage, current and (E) areal power density on external electrical resistance. The error bars represent the mean absolute error from three samples at each velocity or resistance.

(F) Performance comparisons between MSCF-based FFNGs and some recently reported water-based generators; more details can be found in Table S1.

(G) Long-term electrical generation repeatability of a 5-cm-long FFNG over 1000 cycles under 16 cm s^{-1} flow of 0.6 mol L^{-1} NaCl aqueous solution. The insets show FFNG output voltage profiles in the first five and last five cycles.

Figure 3. Electricity generation performance of woven FFNG.

(A) Photograph of a 10-cm-long, woven, FFNG device.

(B) Schematic illustration of the electricity output generated by vertically shifting the woven FFNG device in a 0.6 mol L^{-1} NaCl solution. The woven FFNG device was half-immersed, and its electric output was generated by pulling on the exposed FFNG end.

(C) Output voltage and (D) generated current from a 5 cm height variation of the woven FFNG device in a 0.6 mol L^{-1} NaCl aqueous solution.

(E) Output voltages generated from the woven FFNG device at different velocities and 0.6 mol L^{-1} NaCl aqueous solution.

Figure 4. Mechanism analysis of electricity generation.

(A) Charge distribution model displaying movement of aqueous NaCl solution on the surface of MoS_2 nanosheets.

(B) Zeta potentials of MoS_2 nanosheets, carbon fibers in DI water, 0.6 and 4 mol L^{-1} NaCl aqueous solutions. The error bars represent the mean absolute error from three parallel measurements of each sample.

Charge density differences of Na^+ and Cl^- adsorbed on different surfaces: Na^+ adsorbed on the surface of (C) MoS_2 nanosheets and (E) microcrystal graphite containing 58% sp^3 C; Cl^- adsorbed on the surface of (D) MoS_2 nanosheets and (F) microcrystal graphite containing 58% sp^3 C. The isosurface value was set to 0.007 e/$Å^3$.

Figure 5. Self-powered integrated device and application.

(A) Schematic of a self-powered system that used an energy harvester (FFNG), an energy storage device (MXene belt-based supercapacitor) and a functional device (flexible strain sensor).

(B) Hydrovoltaic charge-galvanostatic discharge curves of the integrated, self-powered device at different discharge currents. Charge time for the FFNG device was 90 s, while voltage output was 540 mV.

(C) Real-time current response of the strain sensor at different deformation states after the integrated device was charged by the FFNG.

(D) A 3.1 V self-powered system, based on the FFNG energy harvester, lighting a green LED. The inset is an enlarged photograph of a lit, green LED.

(E-G) A 3.1 V self-powered system, based on the FFNG energy harvester, powering a digital LCD timer. The insets are enlarged photographs of the LCD screens.

Video caption

Video 1. A self-powered system that uses the energy harvested from a 10-cm-long FENG to power an LCD time-meter for 30 s.