Hyper-stretchable self-powered sensors based on electrohydrodynamically printed, self-similar piezoelectric nano/microfibers

YongAn Huang\textsuperscript{a,b}, Yajiang Ding\textsuperscript{a,b}, Jing Bian\textsuperscript{a,b}, Yewang Su\textsuperscript{c}, Jun Zhou\textsuperscript{d}, Yongqing Duan\textsuperscript{a,b,*}, Zhouping Yin\textsuperscript{a,b,*}

\textsuperscript{a} State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, Wuhan 430074, China
\textsuperscript{b} Flexible Electronics Research Center, Huazhong University of Science and Technology, Wuhan 430074, China
\textsuperscript{c} State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China
\textsuperscript{d} Wuhan National Laboratory for Optoelectronics and School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, China

**ARTICLE INFO**

Keywords:
- Stretchable electronics
- Self-powered sensor
- Electrohydrodynamic printing
- Piezoelectric nanofiber
- Buckling mechanics

**ABSTRACT**

Hyper-stretchable self-powered sensors with high sensitivity and excellent stability using low-cost, printable, organic nanomaterials are attractive for immense applications. Here we present self-similar piezoelectric nano/microfibers for a hyper-stretchable self-powered sensor that demonstrates high stretchability (> 300%), low detection limit (0.2 mg), and excellent durability (> 1400 times at strain 150%). A proposed helix electrohydrodynamic printing technique (HE-Printing) in combination with in-surface self-organized buckling is used to fabricate aligned self-similar polyvinylidene fluoride (PVDF) nano/microfibers with in situ mechanical stretch and electrical poling to produce excellent piezoelectric properties. The hyper-stretchable self-powered sensors have shown repeatable and consistent electrical outputs with detection limit an order of magnitude smaller than the other stretchable sensors. Additionally, such sensors can simultaneously measure the own status and the extra multiply physical quantities, such as lateral pressure, impulse rate and applied strain. The high sensitivity can be further utilized to remotely detect human motion in addition to sensing a piece of paper with 1 mm × 1 mm. Further the fiber-based sensors can avoid the catastrophic collapse or wrinkling of serpentine film-based structure during stretching.

1. Introduction

Stretchable sensor is a field that is rapidly advancing as driven by immense applications including wearable and epidermal electronics [1–5], human-machine interface [6,7], rehabilitation and health monitoring [8], and e-skin [9–12] due to their conformability to curved surfaces and ability to withstand high strain levels. The major success is the judicious and specialized research of the fabrication processes and device designs of highly stretchable architecture. The stretchability has been achieved by utilizing nanomaterials [13–15], rubberlike materials [16,17], liquid metal and conductive liquid [18,19], and serpentine/self-similar/kirigami/bioinspired patterns [20–24]. However, such sensors are commonly fabricated by photolithographic or spin-coating techniques that are either complicated and expensive or incompatible with large-scale, low-cost fabrication. Usually, the inkjet printing and direct-writing techniques were normally suitable for flexible, not stretchable, devices [25–27]. It is significant to develop low-cost printing routes of high-performance, highly stretchable sensors.

In the past decade, the development of stretchable sensors achieved great progresses, including the stretchability, sensitivity, and fabrication [21,28,29]. Many stretchable sensors based on piezoresistive effect were reported, which even has the ability to detect strain up to 280% [13]. However, an external power supply to generate bias voltage was inevitable for these stretchable sensors during the operation and characterization, otherwise none of them can normally work [30,31]. It would increase the device cost and structural complexity considering power consumption. A reported film-based self-powered piezoelectric system could be uniaxially stretched as high as 30% via the serpentine metal lines, however the sensing units were still unstretchable [32]. Stretchable self-powered sensor was introduced by virtue of helix fibers, and the stretchability achieve 25% [33]. Further, a fiber-convolved layout tremendously enlarged the stretchability up to 70% [2]. When the sensors can be stretched further to larger than 100% or even 300%, and have low detection limit, the applications can tremendously expand.

Here, we proposed self-similar piezoelectric nano/microfibers for a...
hyper-stretchable self-powered sensor (HSS) which demonstrated ultra-high mechanical stretchability (> 300%), ultra-low detection limit (< 1 mg), and excellent durability (reciprocating stretch and release > 1400 times at strain 150%). The self-similar Poly(vinylidene-fluoride) (PVDF) nano/microfibers were fabricated by a newly-proposed helix electrohydrodynamic printing (HE-Printing) technique in combination with controllable in-surface self-organized buckling, in a low-cost, large-scale and aligned manner. It can individually manipulate the fiber flying in a helical manner, different from disordered dance of electrospinning and straight line of near-field electrospinning and mechanoelectrospinning [25]. Comprehensive experimental and theoretical studies proved that the HE-Printing technique can directly fabricate various serpentine nano/microfibers. The HSS, unlike film-based sensors, never needs freestanding status to improve stretchability and avoid generating catastrophic out-of-surface deformation [34]. It showed repeatable and consistent electrical outputs with detection limit an order of magnitude smaller than the other stretchable sensors. Besides, it could simultaneously measure the own status and multiply extra mechanical stimuli such as the amplitude and speed of external loading, and keep stable sensing even under different stretching. The HSS was very high sensitive and utilized to remotely detect slight human motion including breathing and walking.

2. Experimental section

2.1. Preparation of PVDF solution and substrates

The PVDF (Kynar 761) was purchased from Arkema Investment Co. Ltd. N,N-dimethylformamide (DMF) and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. All the materials were used directly without further purification. The polymer PVDF (18 wt%) was added in the solvent mixture DMF/acetone (50/50 wt%), and heated at 35 °C for 6 h to make the solution homogeneous.

Two kinds of substrates were adopted, Ecoflex substrate with microchannels and PDMS-on-Ecoflex substrate with excellent stickiness. 1) The Ecoflex solution (Ecoflex 0030, Smooth-On Inc.) was prepared by mixing the base and the curing agent with a ratio of 1:1, and cast into mold with channel pattern before being placed in a vacuum oven to remove air bubbles, then the solution was thermally cured at 60 °C for 10 min 2) For PDMS-on-Ecoflex substrate, Ecoflex solution was spin-coated on glass substrate, followed by thermal curing at 60 °C for 10 min, and the thickness was ~ 0.5 mm. Then PDMS solution (sylgard 184, Dow Corning, Inc.) (mixing the base and the curing agent with a ratio of 10:1) was spin-coated on the Ecoflex substrate and the PDMS layer's thickness is about 0.1 mm. The mixture was first placed in a vacuum oven to remove air bubbles and then thermally cured at 60 °C for 40 min to obtain a half cured PDMS layer.

2.2. Fabrication of self-similar fiber-based sensor

The HE-Printing was utilized to fabricate piezoelectric PVDF nano/microfibers. The PVDF solution was delivered using a syringe pump. A stainless-steel needle (inner and external diameter of 260 µm and 510 µm respectively) was adopted. A high voltage was exerted between nozzle and collector to generate jetting fiber through a power supplier (DW-P403, Dongwen Inc.).

Bidirectionally stretch the PDMS-on-Ecoflex substrate and place it onto silicon substrate with the PVDF nano/microfibers for several minutes, then quickly peel off and slowly release the elastomer to obtain self-similar nano/microfibers. Bond the Ecoflex substrate onto the PDMS-on-Ecoflex substrate with PVDF nano/microfibers to form microstructured channels, followed by injecting liquid metal (EgaIn, 75% gallium and 25% indium) to form stretchable interdigital electrodes. One needs to increase the stickiness between fibers and PDMS surface,
and reduce stickiness between fibers and silicon surface: 1) silane blocking agent was adopted to achieve hydrophobic treatment of silicon substrate, and 2) semi-solidified PDMS-on-Ecoflex substrate was utilized to receive nano/microfibers from silicon substrate.

2.3. Characterization

Infrared Radiation spectroscopy (IR) was performed with a Fourier transform infrared spectroscopy (FTIR) spectrophotometer (Spectrum 116 100, Perkin-Elmer Inc.), equipped with an IR grid polarizer (Specac Limited, UK), consisting of 0.12 mm wide strips of aluminium. A PANalytical X’pert MRD system, with Cu k-alpha radiation (wavelength 0.15418 nm), crossed-slit collimator as primary optics, and a parallel plate collimator as secondary optics, a flat graphite monochromator and a proportional detector, was used for XRD measurements. The crystallinity of fibers was calculated from the area of diffraction peaks divided by the area of the whole diffraction curve. Supplementary Fig. S1a shows FTIR transmission spectrum of polarized fibers under various $U_{\text{applied}}$. Polar $\beta$ phase bands appeared distinctly at 511, 600, 840 and 1275 cm$^{-1}$, while the non-polar $\alpha$ phase bands were not obvious (411, 795, 1402 cm$^{-1}$) [35]. Supplementary Fig. S1b indicated that the concentration of $\beta$ phase $R(\beta)$ increased monotonously with $U_{\text{applied}}$. Infrared spectroscopy absorption bands at 795 and 840 cm$^{-1}$ were chosen to characterize $\alpha$ and $\beta$ phases. The relatively faction of $\beta$ phase was calculated by $F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{K_\beta A_\alpha + A_\beta}$ [36], where, $A_\alpha$ and $A_\beta$ are the absorbance at 795 and 840 cm$^{-1}$, respectively, $X_\alpha$ and $X_\beta$ are the degree of crystallinity of $\alpha$ and $\beta$ phases, and $K_\beta = 6.1 \times 10^5$ cm$^2$/mol and $K_\alpha = 7.7 \times 10^5$ cm$^2$/mol are the absorption coefficients at the respective wave number.

3. Results and discussion

3.1. Architecture of an HSS and HE-Printing technique

An HSS and its exploded view of multilayer construction layout are schematically illustrated in Fig. 1a and b. Specifically, the HSS is based on a sandwich-structured composite, including aligned self-similar nano/microfibers of piezoelectric PVDF and liquid-metal electrode embedded between two layers of different substrates. The HSS can undergo large stretchability such as $\sim 320\%$ (stretched from $\sim 36$ mm to $\sim 154$ mm) and still work very well, as shown in Fig. 1c. Liquid metal, injected into interdigital microchannel with cross-section of $400 \mu m \times 400 \mu m$ embedded in Ecoflex substrate, acts as stretchable electrodes that deform with substrate and provide the stretchability matching with self-similar nano/microfibers. The PDMS-on-Ecoflex substrate utilizes the surface stickiness of fresh PDMS to achieve high bonding strength with nano/microfibers, and the hyperelasticity of Ecoflex to improve the stretchability. Fig. 1d illustrates the fabrication principle of self-similar nano/microfibers. It is a 3-step fabrication process: 1) HE-Printing deposits the initial serpentine nano/microfibers with tunable wavelength of 200–2000 µm and amplitude of 0–500 µm on silicon substrate. 2) The PDMS-on-Ecoflex substrate, stretched by uniaxial/biaxial prestrain $\varepsilon_{\text{prestrain}}$ much larger than the critical strain $\varepsilon_{\text{critical}}$ of nano/microfiber buckling, is pressed down upon the silicon substrate [37]. 3) The PDMS-on-Ecoflex substrate is peeled off, followed by releasing the prestrain for the self-organized buckling of serpentine nano/microfibers to generate a “spring-on-string” self-similar serpentine geometry, as shown in Fig. 1e. All the self-similar nano/microfibers were bonded on the PDMS-on-Ecoflex substrate, followed by covering Ecoflex layer with microchannel for the liquid-metal electrode.

We developed an HE-Printing technique by controlling the “whipping/buckling” instability of the electrical-field-driven jetting nano/microfiber. The helical nano/microfiber accumulated into cylinder in the case of stationary collector (Supplementary Fig. S2), or formed versatile serpentine structures via the linear movement of collector with

---

**Fig. 2. HE-Printing technique for serpentine nano/microfibers.** a) Relationship of the orbit of contact point, the deposited trace and various serpentine microstructures with different $v_{\text{substrate}}/v_{\text{jetting}}$, such as coiled, ‘S’-Fig., and wavy-shaped structures (simulation results and optical images of samples). b) Critical velocity for transformation between various serpentine microstructures, and influence of velocity on wavelength. c) The top three wavy-shaped structures with the same aspect ratio but different size, and the bottom three ones with the similar size but different aspect ratio. d) Optical image of large-scale, aligned, wavy-shape serpentine fiber-array on Si wafer. e) Optical image of large-scale, aligned, self-similar fiber-array on PDMS-on-Ecoflex substrate.
different substrate speeds $V_{\text{substrate}}$ (Fig. 2a), where the applied voltage $U_{\text{applied}}$ was 1.5–3 kV between a needle with inner diameter of 260 µm, fed by a syringe pump at a flow-rate $Q_{\text{flow}}$ of 300–600 nL/min, and a collector at a distance of $h_{\text{nozzle}}$ from 10 mm to 35 mm. The simulation of “whipping/buckling” instability agreed well with experimental observations (Supplementary Text 1), and give the velocity $V_{\text{jetting}}$ of jetting nano/microfiber at the contact point on silicon substrate.

Three key process parameters ($V_{\text{substrate}}$, $U_{\text{applied}}$, and $h_{\text{nozzle}}$) can digitally manipulate the whipping nano/microfiber to form various geometries. 1) Tuning $V_{\text{substrate}}$ can generate four kinds of geometric patterns (coiled fibers, “S”-shaped fibers, wavy-shaped fibers and straight fibers). The laser scanning confocal microscope (LSCM) images in Fig. 2a showed the relationship of the orbit of contact point, the deposited trace and the patterns with the ratio $V_{\text{substrate}}/V_{\text{jetting}}$ by bifurcation theory of liquid ropes (discussed in Supplementary Text 2) [38]. Three critical substrate speeds, dividing four kinds of patterns, were ~130 mm/s, ~230 mm/s and ~360 mm/s, in the case of PVDF of 18% concentration, $U_{\text{applied}} = 2.2$ kV, $h_{\text{nozzle}} = 25$ mm, and $Q_{\text{flow}} = 600$ nL/min. Additionally, $V_{\text{substrate}}$ controlled the wavelength and amplitude of serpentine geometry, as shown in Fig. 2b and Supplementary Fig. 54. 2) $U_{\text{applied}}$ simultaneously increased the jetting speed and helix rotation speed monotonously, and decreased the jetting diameter of deposited coil. 3) $h_{\text{nozzle}}$ was helpful for controlling the non-axisymmetric instability, and formed approximate circle cross-section for in-surface buckling by tuning the solidification time of jetting. Various serpentine structural layouts were formed by digitally tuning the above process parameters, such as serpentine nano/microfibers with the same and various aspect ratios, and large-scale serpentine nano/microfibers, as shown in Fig. 2c and d.

### 3.2. Fabrication of self-similar nano/microfibers

The self-organized buckling of printed serpentine nano/microfibers represents an important approach to achieve excellent stretchability, where the prestrain $\varepsilon_{\text{prestrain}}$ is the driving force of buckling. $\varepsilon_{\text{prestrain}}$, much larger than the in-surface critical strain $\varepsilon_{\text{critical-insurface}}$ of nano/microfibers

$$\varepsilon_{\text{critical-insurface}} = \frac{1}{\varphi} \sqrt{\frac{E_{\text{PDMS}}}{E_{\text{fiber}}} - \frac{1}{A_{\text{fiber}}} - 1},$$

should be applied to the PDMS-on-Ecoflex substrate, where $E_{\text{fiber}}$ and $E_{\text{PDMS}}$ are the Young’s moduli of fiber and PDMS layer, $A_{\text{fiber}}$ is the cross-section area of nano/microfiber, $I_{\text{fiber-insurface}}$ is the inertia moment of nano/microfiber in surface,

$$\varphi = \left(\frac{1}{\beta} - 2\varphi - 2\ln\left(\frac{\gamma}{\beta}\right) - 1\right) \ln\left(\frac{H_{\text{fiber-insurface}}}{W_{\text{fiber-insurface}}}ight),$$

and $E_{\text{PDMS}} = E_{\text{PDMS}}/(1 - \nu_{\text{PDMS}})$, $H$ and $W$ are the height and width of nano/microfiber cross-section [37]. We observed that the cross-section shape of nano/microfiber determines the buckling mode (in-/out-of-surface buckling), and the elastic modulus ratio $E_{\text{PDMS}}/E_{\text{fiber}}$ seriously influences the critical strains of in-surface and out-of-surface buckling modes, respectively, but exerts negligible influence on the transformation between buckling modes [37,39]. The critical aspect ratio of cross-section was predicted as $H/W = 0.9$ at $E_{\text{PDMS}}/E_{\text{fiber}} = 3.3 \times 10^{-4}$. So the nano/microfibers with circle cross-section always buckle in surface, which was proved in our reported experiments [34].

Fig. 2e shows an LSCM image of large-scale, aligned, self-similar nano/microfibers self-organized from serpentine nano/microfibers of Fig. 2d. There were self-similar nano/microfibers with various sizes and similar aspect ratio and with various aspect ratios (Supplementary Fig. S5a and b). The initial serpentine geometry ($\lambda_{\text{initial}}$ and $A_{\text{initial}}$) proportionally shrank to the first-level wavy geometry ($\lambda_{\text{level1}}$ and $A_{\text{level1}}$) of self-similar geometry with the second wavy geometry ($\lambda_{\text{level2}}$ and $A_{\text{level2}}$), namely $\lambda_{\text{level1}} = \lambda_{\text{initial}}/(1 + \varepsilon_{\text{prestrain},x})$ and $A_{\text{level1}} = A_{\text{initial}}/(1 + \varepsilon_{\text{prestrain},x})$, where $\varepsilon_{\text{prestrain},x}$ and $\varepsilon_{\text{prestrain},y}$ are the prestrains along the direction of wavelength and amplitude. $\lambda_{\text{level2}}$ and $A_{\text{level2}}$ are

$$\lambda_{\text{level2}} = \frac{2 \pi}{\lambda_{\text{level1}}},$$

and $A_{\text{level2}} = \frac{A_{\text{level1}}}{\lambda_{\text{level2}}^2}$. The theoretical prediction of $\lambda_{\text{level2}}$ is 59 µm, and agreed well with the finite element simulation (commercial software ABAQUS) (~55 µm) and experiment (~50 µm), where the diameter of nano/microfibers was ~2 µm, $E_{\text{fiber}}$ = 2 GPa, $\nu_{\text{fiber}} = 0.3$, $E_{\text{PDMS}} = 1$ MPa and $\nu_{\text{PDMS}} = 0.45$. It was observed that the second-order serpentine shape was about one-order of magnitude smaller than the initial one. Additionally, the experimental results of Supplementary Fig. S5c show that the prestrain decreased the size of the first-level wavy geometry, and increased the density of the second-level wavy geometry, where the prestrains were 30–120%. The prestrain improved the stretchability of serpentine nano/microfibers with the increment of prestrain, which was proved by the finite element simulation, as shown in Supplementary Fig. S5d. Similarly, the applied strains $\varepsilon_{\text{applied}}$ also changed the shape of self-similar serpentine nano/microfibers, where $\varepsilon_{\text{applied}} = 0\%$, 45% and 80%, as shown in Supplementary Fig. S6.

The amplitude and direction of biaxial prestrain were used to tune the geometric shape of self-similar nano/microfibers. Importantly, the direction of prestrain was capable of controlling the buckling region of the serpentine nano/microfiber. For example, when releasing $\varepsilon_{\text{prestrain},x}$, the second-level wavy appeared on the whole serpentine nano/microfiber with small aspect ratio uniformly, and merely at the peaks and valleys of large aspect-ratio serpentine nano/microfiber merely (Supplementary Fig. S7a). Suppose that the serpentine geometry is made up of a series of gradient line segments. Supplementary Fig. S7b presented the effect of direction of prestrain on the wavelength and amplitude, agreeing very well with the simulation of Supplementary Fig. S7c (the angles are 0°, 30°, 45°, 60°, and 90°). There is a critical angle between the prestrain and nano/microfiber, only below which the buckling appears. And Supplementary Fig. S7d experimentally showed the critical angle was ~55°, which agree well with the theoretical prediction (Supplementary Text 3.1)

$$\delta_1 = \tan^{-1}\left(\frac{\sin(\theta_0)}{1 - \varepsilon_{\text{PDMS}}/\varepsilon_{\text{prestrain}} \cos(\theta_0)} \right),$$

where, $\theta_0$ was resulted from $\theta_0 = \frac{\sin^2(\gamma) + (1 - \cos(\gamma))^2}{\cos(\gamma)} = 1 - \varepsilon_{\text{critical}}$ and $\theta_0$, $\theta_1$, $L_0$ and $L_1$ are the angle and length before and after releasing the prestrain, respectively (Supplementary Fig. S5a).

Supplementary Text 3.1 discussed the relationship of deformation between the nano/microfiber and substrate under uniaxial tensile. Here, we established a calculation law for sinusoidal geometry ($A_{\text{level0}}$ and $\lambda_{\text{level0}}$) for uniform self-similar nano/microfiber. The critical aspect ratio $\beta_{\text{critical}}$ was calculated as $\beta_{\text{critical}} = \frac{A_{\text{level0}}}{\lambda_{\text{level0}}^2} = \frac{\varepsilon_{\text{prestrain}}}{\Phi(\text{prestrain})}$, which is a prestrain-related function, and more details can be found in Supplementary Text 3.2. When the aspect ratio is smaller than $\beta_{\text{critical}}$, the self-similar nano/microfibers can be fabricated. Additionally, Supplementary Text 3.3 established the model under biaxial tensile condition, which demonstrated that the ratio of prestrains in two directions played a critical role in determining the critical angle for buckling. Interestingly, Supplementary Fig. S8c shows the inclined nano/microfibers underwent compression before stretching, and Fig. S8d explained the influence of the ratio of prestrains on buckling.

### 3.3. Characterization of the HSS

HE-Printing in situ electrically polarized PVDF nano/microfibers to transform the basic crystalline phases ($\alpha$ and $\gamma$) into the polar $\beta$ phase, for the generation of piezoelectricity [27]. The polarization monotonically increased with applied voltage, and tended to converge when $U_{\text{applied}} > 1.7$ kV, as shown in Supplementary Fig. S1. The detail characterization between the process parameters and the piezoelectricity was discussed in the Experimental Section. Fig. 3a shows the HSS underwent uniaxial and biaxial stretching, curling and crumpling. Fig. 3b
shows the current output and voltage output under arbitrary crumpling. In durability tests, the output kept stable even after more than 1400 times at the applied strain of 150%, as shown in Fig. 3c, where the HSS was repeatedly stretched and released by a homemade automatic stretcher connected with the semiconductor analysis tester (Supplementary Movie S1).

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.nanoen.2017.07.048.

Fig. 3d shows the current output generated by the uniaxial and biaxial applied strains. The results in red color were the current from uniaxial stretching 120% along x-direction with tensile speed of 20 mm/s, 40 mm/s, 80 mm/s, and 160 mm/s, and the peak current were ~ 2.5 nA, ~ 5 nA, ~ 10 nA, and ~ 20 nA, respectively. And the results in blue color were generated by biaxial stretching 120% with the same tensile load speeds of the red one. The figure declares that the outputs were a linear function of the stretching speed. Fig. 3e shows the outputs under uniaxial and biaxial stretching along x-direction with the uniform motion of 40 mm/s of various strain amplitudes from 40% to 200% with an increment of 40%. The maximum current approximately kept constant for both uniaxial and biaxial stretching. And similar results under stretching can be obtained along y-direction (Supplementary Fig. S9a and b) and biaxial stretching. Fig. 3f plots the relationship of peak current change versus the tensile speed and amplitude of both uniaxial and biaxial stretching. It indicates that the current increased linearly with the tensile speed, and was free from the stretching amplitude. Based on the conclusion, the HSS can be utilized to measure the velocity of movement, without the influence of motion range, which will be further discussed in the next section.

Supplementary Fig. S9c and d show the electrical output under bending by compression in x-direction and y-direction with different compression deformations, at the tensile speed of 40 mm/s. The results indicate that the output was similar by bending with the same speed, even at different strain levels. The HSS can generate electricity under arbitrary twisting (Supplementary Fig. S9e).

3.4. Applications of the HSS

The ability to simultaneously measure the internal status and multiply external mechanical stimuli, such as the lateral pressure, the loading rate and the applied strains of substrate, is crucial for HSSs, which remains a challenge. Fig. 4 shows the measurements of the amplitude (pressure or displacement) and speed (velocity or frequency) of external mechanical stimuli through HSSs in attached and freestanding modes. Fig. 4a is the homemade loading platform, based on CNC-MLM (computer numerical control multi-linkage mechanism). The applied load is calculated by using the Hooke’s law and the deformation of PDMS pad (controlled by CNC-MLM). Fig. 4b shows the current of applied loads with different speeds (frequencies are 1.0 Hz, 1.3 Hz and 1.6 Hz) and the same amplitude (2 mm in experiment) of mechanical stimuli on the covered metal pad. The positive current output was resulted from the springback of soft substrate, which was used to measure the amplitude of mechanical stimuli. The negative current output is a linear increasing function of the speed of mechanical stimuli. The current output is consistent with fundamental piezoelectric theory $i_{\text{fiber}} = d_{33}E_{\text{fiber}}A_{\text{fiber}}E_{\text{applied}}$ [41,42], where $i_{\text{fiber}}$ is the current output, $d_{33}$ is the piezoelectric charge constant, and $E_{\text{applied}}$ is the applied strain rate (proportional to the speed of mechanical stimuli). Conversely, Fig. 4c shows the results of mechanical stimuli with the same speed (1.6 Hz) and different amplitudes (0.8 mm, 1.4 mm and 2 mm). The positive output linearly increases with the amplitude, and the negative output can remain the same due to the same speed. It indicates that the HSS can simultaneously and directly measure the amplitude and speed of mechanical stimuli, based on the positive current and negative current.
Besides, the HSS should never decrease their sensitivity under large stretched state. Fig. 4d shows the output results of the HSS stretched by various applied strains and subjected to the same loading (0.8 mm) in the case of attachment mode. The bottom constant output shows the adoption of the same amplitude of mechanical stimuli, and the peak current denotes the amplitude of mechanical stimuli. However, the upper output linearly increases with the applied strain. The main reason is that the applied strain decreases the thickness and increases the stiffness of the HSS. It improves the springback speed, and thereby enlarges the current. It proved that the HSS not only measured the lateral pressure, but also itself stretched strain. Fig. 4e shows the output results of the HSS under various lateral loadings (0 mm, 4 mm, 8 mm and 12 mm) and applied strains (0%, 50%, 100% and 150%) in freestanding status. The output current was symmetric, different from those asymmetric outputs in the attachment mode. The results indicated that the current was mainly determined by the lateral pressure when $\varepsilon_{\text{applied}} < 100\%$. The current significantly increased when the HSS were stretched up to 150%. So the HSS can be utilized to measure the lateral pressure under $\varepsilon_{\text{applied}} < 100\%$, and can give warning when the HSS stretched beyond the threshold such as 150%. Further, to study the detection limit, the HSS were utilized to sense various small objects. Fig. 4f shows the measurement of falling of different grains in freestanding status. The falling down from 10 cm of nearly spherical grains, including peanut (~0.75 g), soybean (~0.3 g), azuki bean (~0.15 g), mung bean (~50 mg) and sesame (~2.5 mg), was adopted to exhibit the excellent sensing performance. The impact loads, calculated by $F = \sqrt{2g \times m \times t}$, for the five objects are $13.1 \times 10^{-3}$ N, $7 \times 10^{-3}$ N, $4.67 \times 10^{-3}$ N, $1.55 \times 10^{-3}$ N and $2.92 \times 10^{-3}$ N, respectively, where $g$ is the gravitational acceleration, $x$ is the falling distance, $m$ is the mass of the object, and $t$ is the impact time (0.06 s–0.12 s obtained from Fig. 4f). The detail of experiment can be observed clearly in Supplementary Movie S2. The HSS also can detect as small as 0.2 mg objects such as paper with 1 mm × 1 mm as shown in Supplementary Fig. 4.
4. Conclusions

In summary, we proposed a hyper-stretchable self-powered sensor (HSS) based on electrohydrodynamically printed, self-similar nano/microfibers and embedded liquid-metal electrodes. The HSS showed high stretchability (up to 320%), low detection limit (0.2 mg) and excellent stability under reciprocating deformation tests (1400 times at high stretchability (up to 320%), low detection limit (0.2 mg) and excellent stability under reciprocating deformation tests (1400 times at high stretchability (up to 320%), low detection limit (0.2 mg) and excellent stability under reciprocating deformation tests (1400 times at high stretchability (up to 320%), low detection limit (0.2 mg) and excellent stability under reciprocating deformation tests (1400 times at 150%). A new HE-Printing technique was introduced for the fabrication of serpentine/self-similar stretching structures of piezoelectric polymeric materials, in a low-cost, large-scale and aligned manner. The HSS adopted a self-similar design that offers unique, spring-on-spring structures for enhanced stretchability, which is the magnitude of prestrain larger than the initial serpentine nano/microfibers. Experimental and theoretical studies provided guidelines for the design, fabrication and applications of the HSS. Significantly, the HSS showed high sensitivity up to detecting 0.2 mg and multifunctional ability to simultaneously measure their own stretchability and high sensitivity has potential applications in super artificial skin for humanoid robotics, human-machine interfaces, and physiological analysis devices.

Acknowledgments

The authors acknowledge supports from the National Natural Science Foundation of China (51635007, 91323303) and The National Key Research and Development Program of China (2016YFB0401105). The general characterization facilities are provided by the Flexible Electronics Manufacturing Laboratory in Comprehensive Experiment Center for Advanced Manufacturing Equipment and Technology at Huazhong University of Science and Technology.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2017.07.048.

References

[1] X. Pu, M. Liu, X. Chen, J. Sun, C. Du, Y. Zhang, J. Zhai, W. Hu, Z.L. Wang, Sci. Adv. 3 (2017) e1700015.
[2] X. He, Y.L. Zh, H.Y. Gou, H.W. Zheng, Y. Xi, C.S. Wu, J. Wang, W. Zhang, C.H. Lu, Z.L. Wang, Adv. Funct. Mater. 27 (2017) 201604378.
YongAn Huang received the B.S. degree (2001), M.S. degree (2004) and Ph.D. degree (2007) from the Northwestern Polytechnical University, Xian, China. Since 2007, he has been a Faculty member at the State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology (HUST), where he became a professor in 2014. His research interests include flexible electronics manufacturing and advanced printing.

Yajiang Ding received his B.S. degree from Huazhong University of Science and Technology (HUST) in 2013. He is now a Ph.D. candidate in the State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, HUST. His research is focused on mechano-electrospinning and organic thin-film transistor for flexible electronics manufacturing.

Jing Bian received his B.S. degree from Huazhong University of Science and Technology (HUST) in 2015. He is now a Ph.D. candidate in the State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, HUST. His research is focused on laser lift-off technique for flexible electronics manufacturing.

Yewang Su received the Ph.D. degree in engineering mechanics from Tsinghua University, Beijing, China, in 2011. He was a post-doctoral fellow with Departments of Civil and Environmental Engineering and Mechanical Engineering, Northwestern University, Evanston, IL, US, from 2011 to 2014. He is currently a research fellow in State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing, China. His research interests include Gas shale, Stretchable electronics and Biomechanics.

Jun Zhou received his B.S. degree in Material Physics (2001) and his Ph.D. in Material Physics and Chemistry (2007) from Sun Yat-Sen University, China. During 2005–2006, he was a visiting student in Georgia Institute of Technology. After he obtaining his Ph.D., He worked in Georgia Institute of Technology as a research scientist. He joined in Wuhan National Laboratory for Optoelectronics (WNOL), Huazhong University of Science and Technology (HUST) as a professor from the end of 2009. His main research interest is flexible energy harvesting and storage devices for self-powered micro/nanosensor systems.

Yongqing Duan received the B.S. and Ph.D. degrees from Huazhong University of Science and Technology (HUST), Wuhan, China, in 2010 and 2015 respectively. She is now a postdoctoral fellow in the State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, HUST. Her research interests include flexible electronics manufacturing and electrohydrodynamic printing.

Zhouping Yin received the B.S. and Ph.D. degrees in mechanical engineering from Huazhong University of Science and Technology (HUST), Wuhan, China, in 1994 and 2000, respectively. He is a professor in school of mechanical science and engineering, HUST. He was awarded the China National Funds for Distinguished Young Scientists in 2006. He is a “Cheung Kong” Chair Professor of HUST since 2009. His research interests include electronic manufacturing equipment and technology, RFID technology and applications, digital manufacturing and applications.
Supporting Information

Hyper-stretchable self-powered sensors based on electrohydrodynamically printed, self-similar piezoelectric nano/microfibers

YongAn Huang\textsuperscript{a,b}, Yajiang Ding\textsuperscript{a,b}, Jing Bian\textsuperscript{a,b}, Yewang Su\textsuperscript{c}, Jun Zhou\textsuperscript{d}, Yongqing Duan\textsuperscript{a,b,*}, Zhouping Yin\textsuperscript{a,b,*}

\textsuperscript{a} State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, Wuhan, 430074, China
\textsuperscript{b} Flexible Electronics Research Center, Huazhong University of Science and Technology, Wuhan, 430074, China
\textsuperscript{c} State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing, 100190, China.
\textsuperscript{d} Wuhan National Laboratory for Optoelectronics and School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, 430074, China

* Corresponding authors.
E-mail addresses: duanyongqing@hust.edu.cn (Y. Duan), yinzhp@mail.hust.edu.cn (Z. Yin).
Text 1 Simulation of electrospinning jet

The driven force is the combination of ‘pull’ driving force from electrical field and ‘push’ counterforce from substrate, which are able to be tuned by the applied voltage and the speed of substrate, respectively. Numerical simulations of the coiling phenomenon in helix electrohydrodynamic printing (HE printing) are conducted using the discrete viscous threads method. The viscous thread is discretized as a polyline, a mass $m_i$ is assigned to each vertex $i$, forces are set upon these masses, and the motion of each mass is obtained by time integration of the fundamental law of dynamics, namely

$$m_i \frac{\partial \mathbf{u}_i}{\partial t} = f_{i, \text{internal}} + f_{i, \text{external}}$$

(1)

where $\mathbf{u}_i$ is the velocity vector of the vertex $i$, $t$ is time, $f_{i, \text{internal}}$ and $f_{i, \text{external}}$ are the internal viscous force obtained from adjacent nodes and the external electric force determined by electric filed and charge on node. Gravity and surface tension are neglected here as they are relatively small compared to electric field force.

The internal viscous force can be captured by means of an energy method\cite{1} that

$$f_{i, \text{internal}} = -\frac{\partial W_i}{\partial \mathbf{u}_i} = -\mathbf{D}_i(\mathbf{r}, \mu, m, a) \cdot \mathbf{u}_i$$

(2)

where $W_i$ is the sum energy of stretch, twist and bend when the spinning jet moves and deforms, $\mathbf{D}_i$ is a matrix which is relative to the jet coordinate $\mathbf{r}$, viscosity $\mu$, radius $a$, and mass $m$.

The external electric force $f_{i, \text{external}}$ is determined by electric filed and charge on node. The high voltage in electrospinning is exerted between nozzle and collector, the vertical downward nonuniform electric filed just below the nozzle can be written as\cite{2}
where $z_i$ means the normal distance between node $i$ and the collector, $H$ means the nozzle-to-collector distance, $U$ means the applied voltage, and $r$ is the radius of the nozzle.

The external electric force can be written as

$$f_{\text{external}} = q_i E_i$$

where $\varepsilon, \varepsilon_0$ means the dielectric constant of the solution, $a_i$ and $l_i$ mean the radius and length of the discrete jet.

When the jet fly from nozzle to collector, it evaporates and solidifies which make the jet mass decrease and viscosity increase

$$\frac{\partial m_i}{\partial t} = k \cdot 2\pi a_i l_i$$

$$\frac{\mu_i}{\mu_0} = 10^{\left[\ln(C_i/C_0)\right]}$$

where $k$ is an evaporation coefficient relative to temperature and humidity et al. $2\pi a_i l_i$ means the surface area of the jet. $\mu_i$ and $\mu_0$ are the real-time and initial viscosity of the jet, $C_i$ and $C_0$ are the real-time and initial concentration of the jet.

We first calculate the internal force through Eq. 2 and the external electric force through Eq. 4, then take these two forces into Eq. 1, meanwhile considering the evaporation/solidification through Eq. 5. By adopting appropriate boundary conditions (nozzle and collector), the coiling behavior of the electrospinning jet can be successfully simulated.

Fig. S3a shows the simulation result of the electrospinning jet when the applied voltage
Submitted to Nano Energy

\[ U_{\text{applied}} = 2 \text{kV}, \text{nozzle-to-substrate distance } h_{\text{nozzle}} = 30 \text{ mm}, \text{The flow rate } Q_{\text{flow}} = 400 \text{ nl/min}, \]

the initial jet radius \( a_0 = 20 \mu\text{m}, \) initial jet velocity \( U_0 = Q / \pi a_0^2, \) initial concentration \( C_0 = 0.18, \) initial viscosity \( \mu_0 = 13 \text{ Pa}\cdot\text{s}. \) The solution density \( \rho = 1000 \text{ kg/m}^3, \) the relative dielectric constant of the solution \( \varepsilon_r = 10, \) the evaporation coefficient \( k = 0.08. \)

Fig. S3b shows the coiling of the lowermost part of the jet in one cycle. Blue line means jet in air while red line means deposited fiber on substrate. The jet in air has very long, straight “tail” and rather short, curvy “coil”. The deposited fibers on substrate form relatively regular circles with diameters of about 160 \( \mu\text{m}, \) and the cycle of the coiling is about 1.2 ms. These parameters are the same order of magnitude with experiment. The velocity of the jet can be divided into downward velocity \( v_z \) and horizontal velocity \( v_{xy}. \) The critical velocity when approaching collector is marked \( v_{\text{jetting}} \) as shown in Fig. S3c, which is a key parameter in pattern transformation. The diameter of the jet decreases rapidly when it just leaves the nozzle, then become much slower and almost stopped decreasing when gradually approaching substrate as shown in Fig. S3d.

Text 2 Critical speed and transformation of patterns of deposited fibers

The deposited trace of the jetting fiber on collector, namely the patterns of meander, alternating loops and translated coiling et al., is a combination of the orbit of the contact point (regular coiling when collector is static) and the movement of the collector. As the jet falling speed \( v_{\text{jetting}} \) and the collector speed \( v_{\text{substrate}} \) do not match (\( 0 \leq v_{\text{jetting}} \leq v_{\text{substrate}} \)), the lower part of the thread will buckle and form a heel shape. Let \( s \) be the arc-length along the trace, \( s = 0 \)
and \( s = v_{\text{jetting}}t \) correspond to the initial point and current point that contact the moving collector. Assume that at the time of \( s/v_{\text{jetting}} \), a point which has an arc-length of \( s \) begin to contact the collector, then it moves with collector and its position at time \( t \), namely the deposited trace \( q(s, t) \) can be written as \[ q(s, t) = r(s) + v_{\text{substrate}}\left(1 - \frac{s}{v_{\text{jetting}}}\right)e_x \quad (6) \]

where \( r(s) \) means the contact position at time \( s/v_{\text{jetting}} \), \( v_{\text{substrate}}(t - s/v_{\text{jetting}})e_x \) means the vector that the contact point moves with the collector.

When derivative \( q(s, t) \) with arc-length \( s \), one can get

\[
\frac{\partial}{\partial s} q(s, t) \bigg|_{s=v_{\text{jetting}}} = r'(s) - \frac{v_{\text{substrate}}}{v_{\text{jetting}}} e_x \quad (7)
\]

where, \( t(s) \) and \( r'(s) \) are the unit tangents of the deposited trace \( q(s, t) \) and orbit of the contact point \( r(s) \), respectively.

Eq.\( (7) \) is based on Cartesian coordinate \((e_x, e_y)\), rewrite it with a polar coordinate \((e_r, e_\psi)\), then we can get

\[
r' = \cos(\theta - \psi) + \frac{v_{\text{substrate}}}{v_{\text{jetting}}} \cos \psi

\]

\[
\psi' = \frac{1}{r} \left( \sin(\theta - \psi) - \frac{v_{\text{substrate}}}{v_{\text{jetting}}} \sin \psi \right) \quad (8)
\]

where, the concrete meaning of \( \theta \) and \( \psi \) can be seen in reference\([4]\).

The curvature \( \theta' = \kappa(r, \psi) \) at the bottom of the hanging thread can be found by fitting DVR simulations, and the approximated fitting function is

\[
\theta' = \sqrt{r} \left( 1 + \frac{0.715^2 \cos(\theta - \psi)}{1 - 0.715 \cos(\theta - \psi)} r \right) \sin(\theta - \psi) \quad (9)
\]

Eqs. (8) and (9) are a set of coupled ordinary nonlinear differential equations for the
functions of \( r(s) \), \( \psi(s) \), \( \theta(s) \), and a dimensionless parameter \( \frac{v_{\text{substrate}}}{v_{\text{jetting}}} \). When varying \( \frac{v_{\text{substrate}}}{v_{\text{jetting}}} \left( \frac{v_{\text{substrate}}}{v_{\text{jetting}}} \in [0,1] \right) \), we can get the solutions of \( r(s) \), \( \psi(s) \), \( \theta(s) \), and then the deposited trace \( q(s, t) \) and the orbit of the contact point \( r(s) \). When collector is motionless \( \left( \frac{v_{\text{substrate}}}{v_{\text{jetting}}} = 0 \right) \), the orbit of contact point is a regular circle with diameter of \( 2R_c \). Continuously increasing \( \frac{v_{\text{substrate}}}{v_{\text{jetting}}} \), translated coiling, alternating loops, W-shaped pattern and wavy-shaped appear in succession, the four typical periodic orbits and corresponding patterns are listed in Fig. 2a. The coordinates \( x/R_c \) and \( y/R_c \) are dimensionless, where \( R_c \) means the regular coiling radius.

Text 3 The effect of prestrain on the buckling

3.1 Uniaxial tensile for buckling

Fig. S8 shows the relationship of deformation between the fiber and substrate before and after releasing prestrain.

1) The uniaxial prestrain is applied on the Ecoflex substrate, as shown in Fig. S8a. Suppose that the initial length of PVDF fiber is \( L_0 \), the angle between the fiber and the direction of strain is \( \theta_0 \), and the substrate is prestrained along horizontal direction. The projections of fiber on x and y directions are \( L_0 \cos(\theta_0) \) and \( L_0 \sin(\theta_0) \) respectively.

2) The deformation of PVDF fiber is determined by the motion of substrate. Releasing the prestrain \( \varepsilon_{\text{prestrain}} \) in the assumption of linear elasticity, the length and width of the substrate become

\[
\frac{L_0 \cos(\theta_0)}{1 + \varepsilon_{\text{prestrain}}} \quad \text{and} \quad \frac{L_0 \sin(\theta_0)}{1 - \nu_{\text{PDMS}} \varepsilon_{\text{prestrain}}},
\]

where \( \nu_{\text{PDMS}} \) is the Poisson's ratio.

3) The final length of PVDF fiber is \( L_1 \) which is determined by the final size of the substrate, the angle between the fiber and the direction of strain is \( \theta_1 \), as shown in Fig. S8a. One can write the length \( L_1 \) and the angle \( \theta_1 \) as
\[ L_1 = \sqrt{\left( \frac{L_0 \cos(\theta_0)}{1 + \varepsilon_{\text{prestrain}}} \right)^2 + \left( \frac{L_0 \sin(\theta_0)}{1 - \nu_{\text{PDMS}} \varepsilon_{\text{prestrain}}} \right)^2} \]  

(10)

\[ \theta_1 = \tan^{-1} \left( \frac{\sin(\theta_0)}{1 - \nu_{\text{PDMS}} \varepsilon_{\text{prestrain}} \cos(\theta_0)} \right) \]  

(11)

The length ratio \( L_1/L_0 \) denote the degree of compression/tensile of fiber which can be adopted to determine whether the fiber is compressed.

\[ \frac{L_1}{L_0} = \sqrt{\left( \frac{\cos(\theta_0)}{1 + \varepsilon_{\text{prestrain}}} \right)^2 + \left( \frac{\sin(\theta_0)}{1 - \nu_{\text{PDMS}} \varepsilon_{\text{prestrain}}} \right)^2} \]  

(12)

For circular or square cross-section, the critical buckling strain or the minimum strain for in-surface buckling is\[^5\]

\[ \varepsilon_{\text{critical}} = \frac{W^2}{A} \sqrt{\frac{E_{\text{PDMS}}}{E_{\text{fiber}}} \sqrt{\frac{I_{\text{fiber}}}{W^4}}} \left( 1 + \frac{1}{2} \frac{2\pi}{5 - 2\gamma - 2 \ln \frac{5}{7} + 2 \ln 2 - \frac{1}{2} \ln \frac{E_{\text{PDMS}}}{E_{\text{fiber}}} + 1 \ln \frac{I_{\text{fiber}}}{W^4} } \right) \]  

(13)

where, \( \frac{E_{\text{PDMS}}}{1 - \nu_{\text{PDMS}}^2} \) is the plane strain modulus of substrate, \( E_{\text{PDMS}} \) is the elastic modulus of the substrate, \( \gamma = 0.577 \) is Euler’s constant and \( W \) is the width of the interfacial contact region, \( I_{\text{fiber}} \) represents the moment of inertia.

When \( \sqrt{\frac{E_{\text{PDMS}}}{E_{\text{fiber}}}} = 0.025 \) (\( E_{\text{fiber}} = 2 \text{ GPa for PVDF, and } E_{\text{PDMS}} = 1 \text{ Mpa, } \nu_{\text{PDMS}} = 0.45 \) for PDMS substrate), \( W = 2 \mu\text{m (square section), the specific critical strain } \varepsilon_{\text{critical}} = 0.0091. \) We can transform the critical strain into the critical degree of compression of fiber \( (L_1/L_0)_{\text{critical}} = 1 - \varepsilon_{\text{critical}} = 0.9909, \) which is validated by finite element simulation.

In a word, the buckling may appear on the condition that the degree of compression of fiber is smaller than the critical length ratio. Namely, \( (L_1/L_0) < (L_1/L_0)_{\text{critical}}. \)

### 3.2 Critical geometry for uniform buckling of serpentine structure

It can be observed from Fig. 2c that the deposited fibers have various
amplitude-wavelength ratio. There exists a critical ratio for the serpentine fibers to generate self-similar fibers that the small wavy can distribute anywhere. The geometry of serpentine fiber is like sinusoidal curve, which can be be characterized by the equation: \( y = A_{\text{level0}} \sin(2\pi x/\lambda_{\text{level0}}) \), where the \( A_{\text{level0}} \) and \( \lambda_{\text{level0}} \) are the amplitude and wavelength of origin deposited serpentine fibers. As showing in Fig. S7 that there exists a critical angle for buckling, so the self-similar serpentine fibers will distribute evenly on the condition that the angel of the maximal gradient in the origin sinusoidal curve is smaller than the critical angle for buckling under a specific prestrain, namely \( \max(dy/dx) < \tan(\theta_0-\text{critical}) \). The critical aspect ratio \( \beta_{\text{critical}} = A_{\text{level0}}/\lambda_{\text{level0}} = \max(dy/dx) = \tan(\theta_0-\text{critical})/2\pi \) is determined by critical angle \( \theta_0-\text{critical} \) which is related with the prestrain applied. As described above, the \( \theta_0-\text{critical} \) can be derived from the condition that \( (L_1/L_0) < (L_1/L_0)_{\text{critical}} \). Using Eq. (12), one can get \( \theta_0-\text{critical} \), and the critical aspect ratio \( \beta_{\text{critical}} = A_{\text{level0}}/\lambda_{\text{level0}} = q(e_{\text{prestrain}})/2\pi \sqrt{1-q^2(e_{\text{prestrain}})} \), where \( q \) denotes:

\[
q = \sin(\theta_{0-\text{critical}}) = \sqrt{\left(1 + e_{\text{prestrain}}\right)^2 \left(1 - \nu_{\text{PDMS}} e_{\text{prestrain}}\right)^2 \left(1 - e_{\text{critical}}\right)^2 - \left(1 - \nu_{\text{PDMS}} e_{\text{prestrain}}\right)^2 \left(1 + e_{\text{prestrain}}\right)^2 \left(1 - \nu_{\text{PDMS}} e_{\text{prestrain}}\right)^2}
\]

(14)

The second level serpentine shape appears only at the peaks and valleys when a uniaxial prestrain is applied along the wavelength direction with \( \beta > \beta_{\text{critical}} \) as shown in Fig. S7 when the aspect ratios is 1.

### 3.3 Biaxial tensile for buckling

In Fig. S8b, supposed the applied strains along \( x \) and \( y \) direction are \( e_{\text{prestrain-x}} \) and \( e_{\text{prestrain-y}} \) respectively. The two applied strains are independent, and the ratio is \( \varphi = e_{\text{prestrain-x}}/e_{\text{prestrain-y}} \). After releasing the prestrain, the lengths of the sides of the rectangle substrate become

\[
\frac{L_0 \sin(\theta_0)}{1 + e_{\text{prestrain-y}}} \quad \text{and} \quad \frac{L_0 \cos(\theta_0)}{1 + e_{\text{prestrain-x}}} = \frac{L_0 \cos(\theta_0)}{1 + \varphi e_{\text{prestrain-y}}}, \text{ respectively. Then one can get}
\]

\[
\frac{L_1}{L_0} = \sqrt{\left(\frac{\sin(\theta_0)}{1 + e_{\text{prestrain-y}}}\right)^2 + \left(\frac{\cos(\theta_0)}{1 + \varphi e_{\text{prestrain-y}}}\right)^2}
\]

(14)

It can be noted from Eq.(14) that the degree of compression is related with \( \theta_0, e_{\text{prestrain-y}}, \) and...
φ. Namely, the buckling of the fiber is determined by \( \theta_0 \), \( \varepsilon_{\text{prestrain-}\gamma} \), and \( \phi \). It is clear from Fig. S8d that when \( \phi = 1 \) (the equal prestrain in two directions), the buckling of fiber is not influenced by the angle, when \( \phi = -\nu_{\text{PDMS}} = -0.45 \) (the substrate is merely stretched in the \( x \)-direction), the condition degenerates into the uniaxial tensile status. The critical angle is seriously affected by the ratio \( \phi \).

References

[1] B. Audoly, N. Clauvelin, P. T. Brun, M. Bergou, E. Grinspun, M. Wardetzky, Journal of Computational Physics 2013, 253, 18.
[2] R. Coelho, J. Debeau, Journal of Physics D: Applied Physics 1971, 4, 1266; N. Bu, Y. Huang, Y. Duan, Y. Ding, Z. Yin, AIP Advances 2015, 5, 017138.
[3] B. Audoly, N. Clauvelin, P.-T. Brun, M. Bergou, E. Grinspun, M. Wardetzky, Journal of Computational Physics 2013, 253, 18.
[4] P. T. Brun, B. Audoly, N. M. Ribe, T. S. Eaves, J. R. Lister, Physical Review Letters 2015, 114, 174501.
[5] Y. Q. Duan, Y. A. Huang, Z. P. Yin, Journal of Physics D-Applied Physics 2015, 48.
Fig. S1. FTIR transmission spectrum of PVDF nanofibers. (a) Transmission of PVDF with applied voltage between nozzle and substrate; (b) The relatively faction of the β phase with applied voltage between nozzle and substrate.
Fig. S2. The ‘whipping/buckling’ instability in HE printing. (a) Schematic diagram of the ‘whipping/buckling’ instability phenomenon of the electrospun jet. (b) Photographs of the electrospun jet coils which heap up above collector until collapse. (c) Photographs of the electrospun jet above collector in one coil cycle.
Fig. S3. The coil-whipping of HE printing. (a) Simulation of the electrospun jet with long, straight “tail” and short, curvy “coil”. (b) Simulation results of the shape of the lowermost part of the jet coils over time. (c) Velocity of the electrospun jet from nozzle to collector. (d) Diameter of the continuous jet from nozzle to collector.
Fig. S4. Wavelength and amplitude of different buckling patterns. (a) Experiment results of the amplitude of the different electrospun patterns varies over collector speed. (b)-(c) Theoretical results of the wavelength (b) and amplitude (c) of different buckling patterns varies over speed match ratio $v_{\text{substrate}}/v_{\text{jetting}}$. 
Fig. S5. Self-similar fibers and their stretchability analysis. (a-b) Self-similar structures with different sizes and shapes. (c) Self-similar structures generated under different prestrains. (d) Simulation results of the maximum strain for different structures while been stretched, where $m$ is the ratio of amplitude (from 200μm to 600μm) and wavelength (fixed 1000μm) of the structure.
**Fig. S6.** The shape geometry of self-similar fiber under various applied strains. The 2D and 3D LSCM images of the shape geometry of self-similar fiber with applied strain of (a) 0%, (b) 45%, and (c) 80%. The left column is optical image of practical deformation, the middle one is magnification of the left one, and the right one is corresponding 3D image. The second-level waves become large and sparse, and finally evolve to the initial wave when the applied strain is equal to the prestrain. The 3D views show the fibers always deform in surface.
Fig. S7. The effect of the angle of prestrain on buckling. (a) The comparison of buckling behavior between the experiment and simulation of wavy-shaped fiber with various aspect ratios under uniaxial stretching. The aspect ratios are 0.1, 0.5, and 1. (b) The experimental result of the buckling behavior of a series of straight fibers with various gradients after releasing the prestrain 20%. (c) The finite element simulation of straight fibers with various gradients after releasing the prestrain 10%. (d) The critical angle for buckling is about 55° for the 20% prestrain, which agrees with the theoretical result very well.
Fig. S8. The relationship of deformation between the fiber and substrate under (a) uniaxial tensile and (b) biaxial tensile. (c) The strain of fiber is related with the prestrain and the initial angle, where the initial angles are 52.5°, 50°, 47.5°, 45°, and 42.5°, and (d) the deformation of the fiber related with the angle, where the substrate is stretched by different ratio of prestrain, and the prestrain at x direction is 30%.
Fig. S9. The electrical output of various motions, including: (a) the stretching speed at the case of tensile strain of $\epsilon_{\text{prestrain-y}} = 120\%$ along y-direction; (b) the tensile strain under the same stretching speed of 40mm/s in y-direction; (c) bending by compression in x-direction under 40mm/s; (d) bending by compression in y-direction under 40mm/s; (e) twist; (f) pressure at the case of various applied strains of 0%, 40%, 80%, 120%, 160%, and 200%.
**Fig. S10.** The electrical output when papers with different weights falling on HSS: (a) the scraps of paper utilized in experiments; and (b) the generated electrical outputs.