Supplementary information for:

Non-wrinkled, highly stretchable piezoelectric devices by electrohydrodynamic direct-writing

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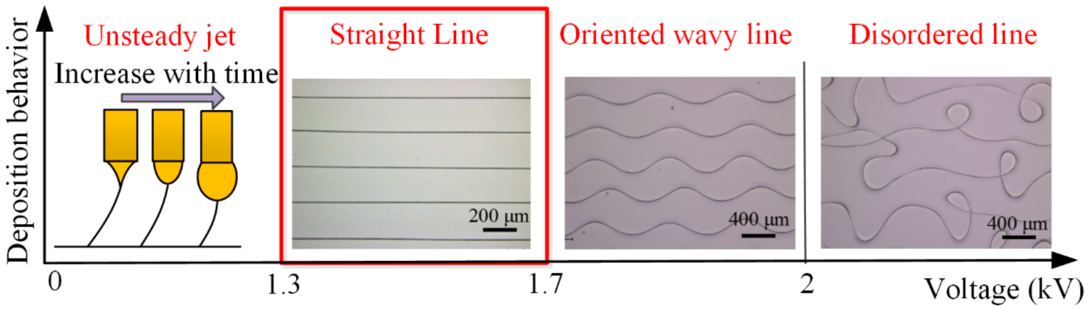

Figure S1. Four stages of MES with the increase of voltage. The distance between nozzle and collector is 4 mm, the speed is 400 mm/s. The first one represents an unsteady situation that the hanging drop continuously increases with time. The following three optical microscopy photographs represent three steady stages and the corresponding deposited fibers (straight fibers, oriented wavy fibers and disordered non-woven fibers) on substrate with the increase of voltage (electric force).

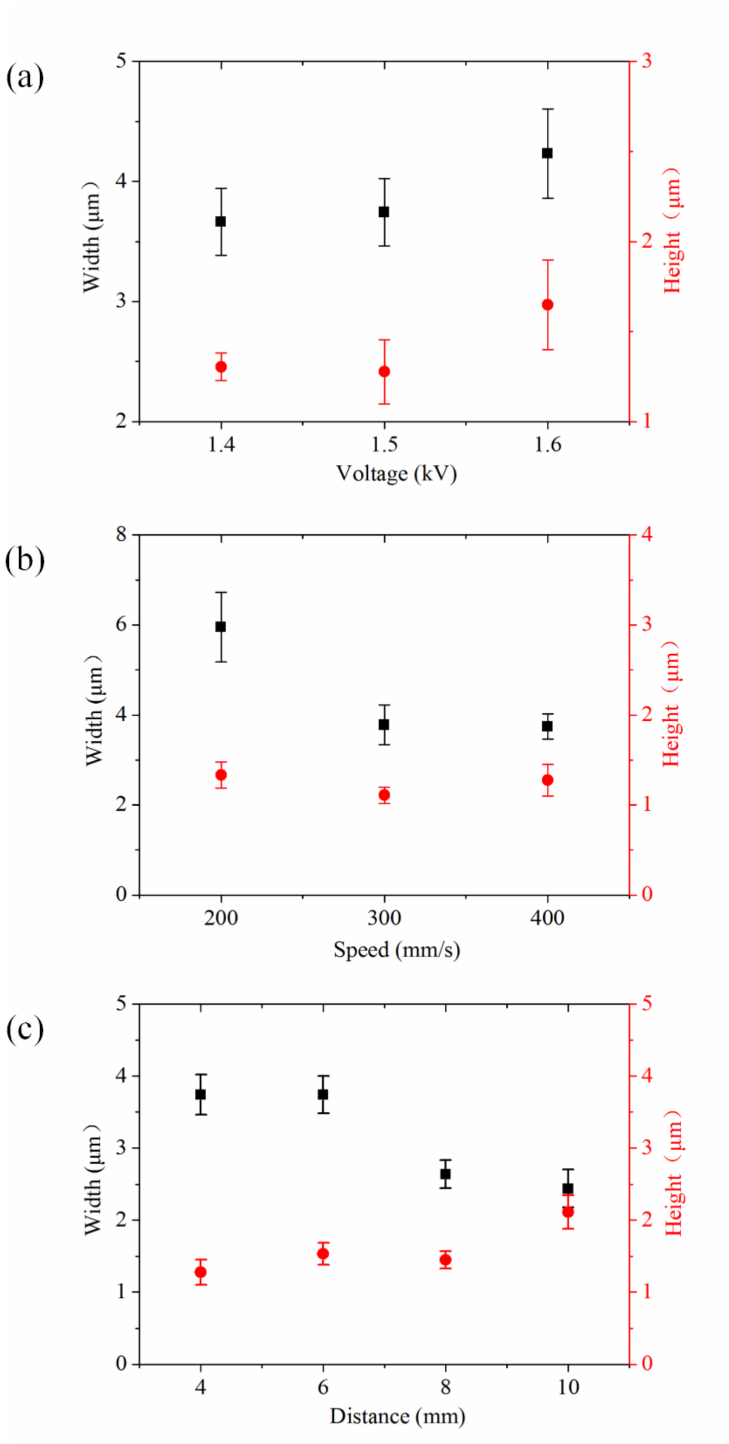

Figure S2. Electrospun fiber's width and height vs voltage, speed and distance. For (a), the distance is 4 mm, and the speed is 400 mm/s. For (b), the distance is 4 mm, and the voltage is 1.5 kV. For (c), the voltage is 1.5 kV, and the speed is 400 mm/s.

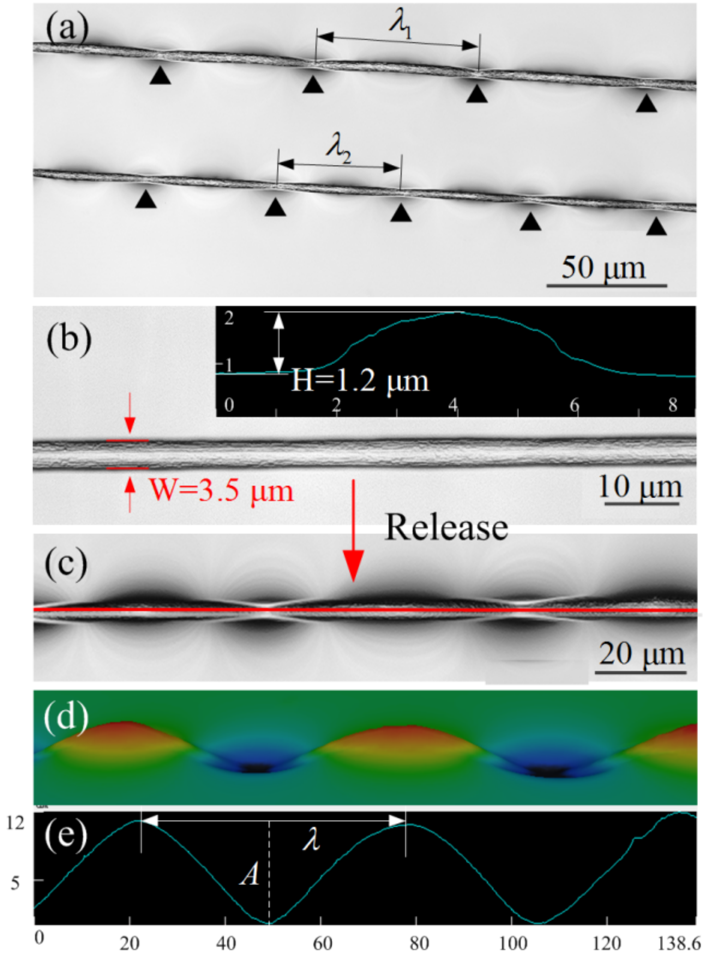

Figure S3. Out-of-surface buckled fibers. (a) Two fibers having different width and height form out-of-surface buckling with different wavelengths (every triangle means a valley). (b) and (c) represent a fiber on PDMS substrate before and after releasing. (d) and (e) are 3D view and sectional view of the out-of-surface buckled fiber.

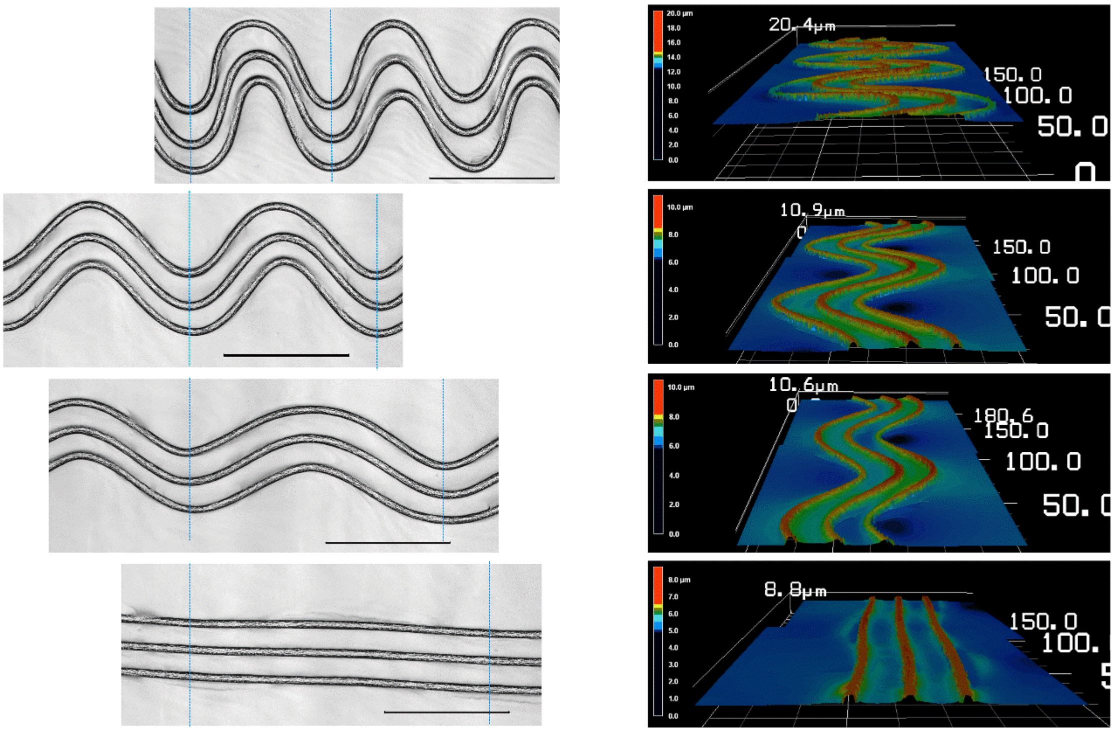

Figure S4. Conformal behavior of in-surface buckled fibers under different applied strains. The right column shows the 3D views of the left. The applied strains are 0%, 40%, 80%, 100% from up to bottom. The black bars represents 50 μm.

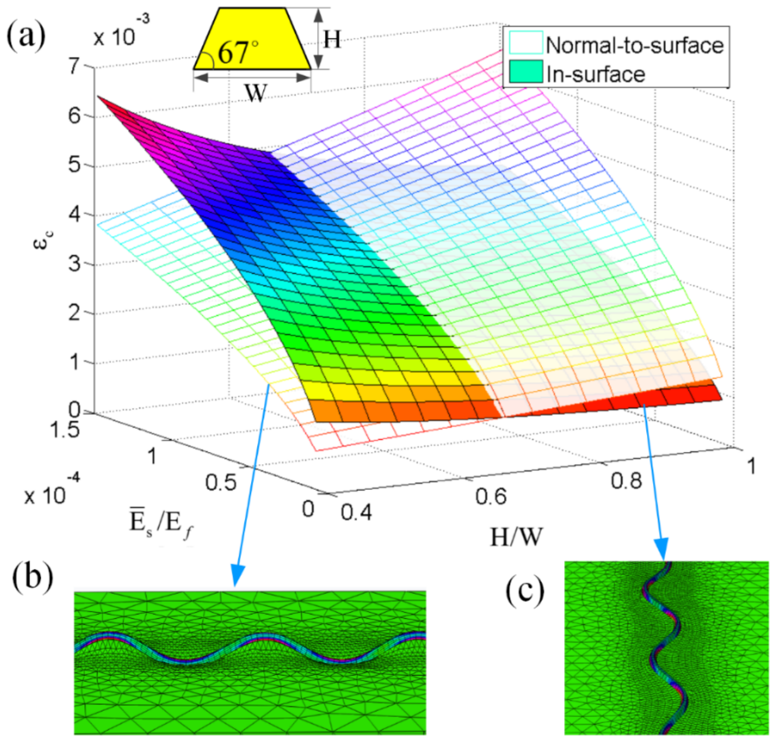

Figure S5. Theoretical studies of the buckling behavior of fibers having isosceles trapezoid cross-sections (67° interior angle). (a) The critical buckling strains for in-surface and normal-to-surface buckling. (b) and (c) are two simulation results which represent two buckling modes.

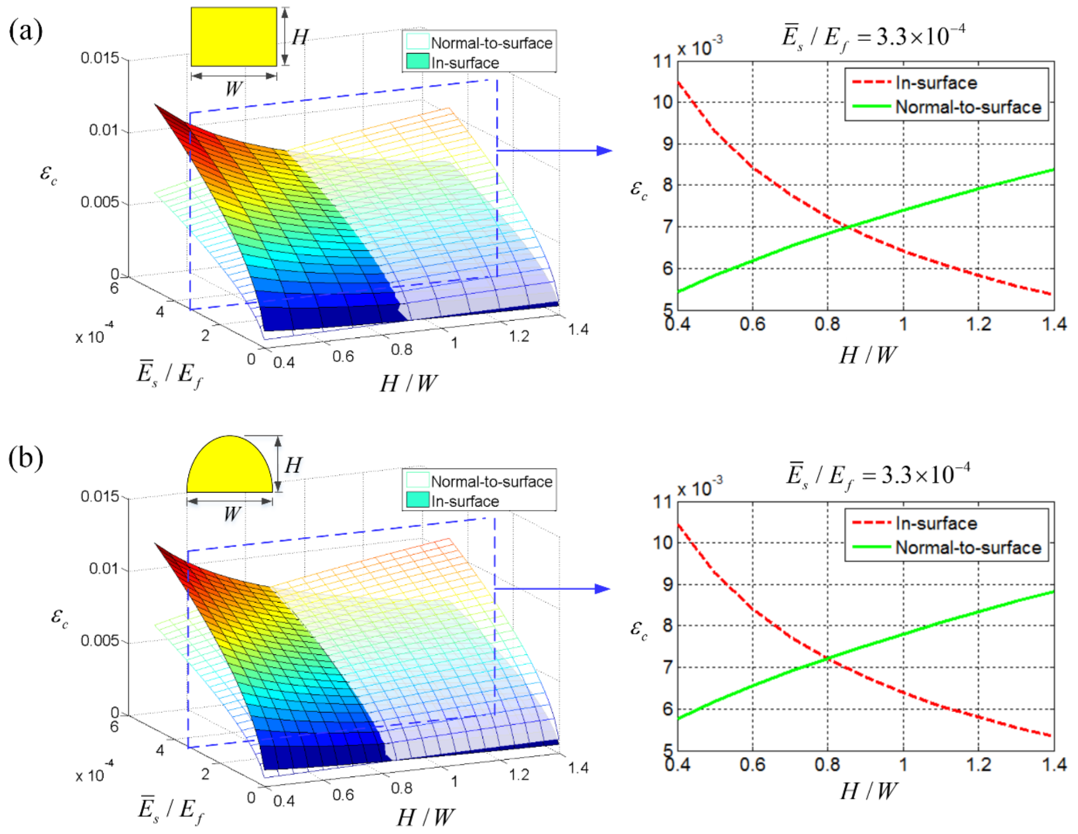

Figure S6. The critical in-/normal-to-surface buckling strains for rectangular sections (a) and semi-elliptical sections (b). The right column represents the critical strain when $\bar{E}_S / E_f = 3.3\times10^{-4}$.

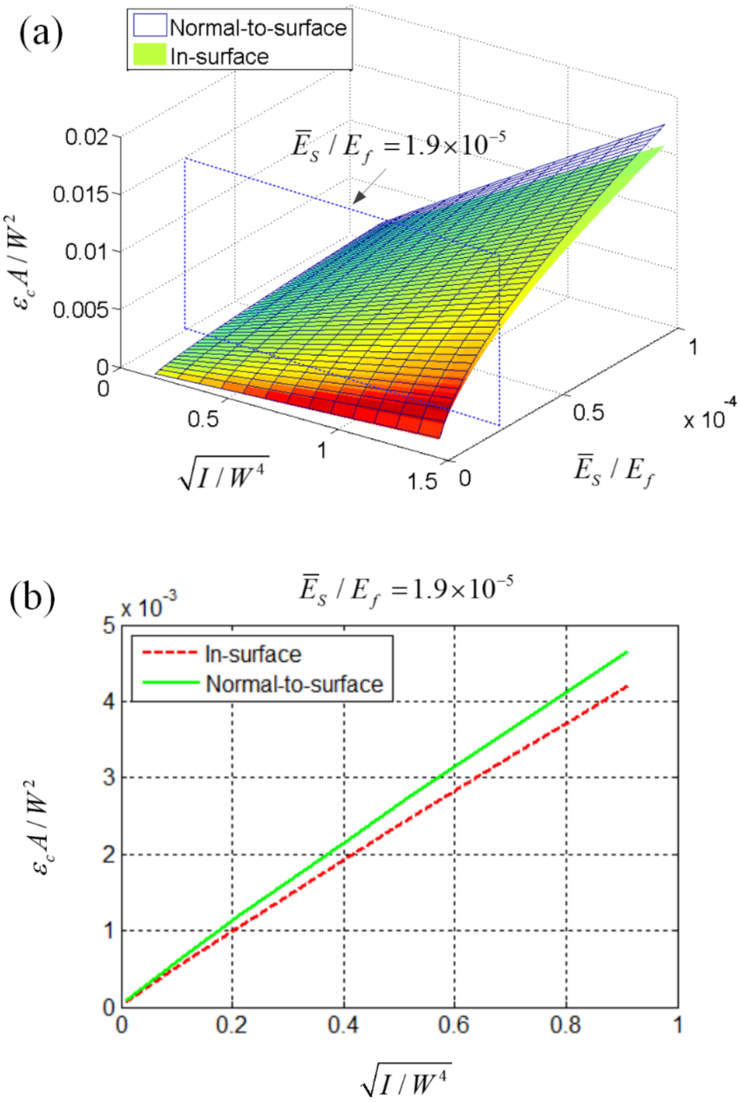

Figure S7. The critical strains for sections having equal moment of inertia in two buckling directions. (a) The critical strains for both in-surface and normal-to-surface buckling when $I_{insurface} = I_{normal}$. (b) The critical strains when $\bar{E}_S / E_f = 1.9\times10^{-5}$.

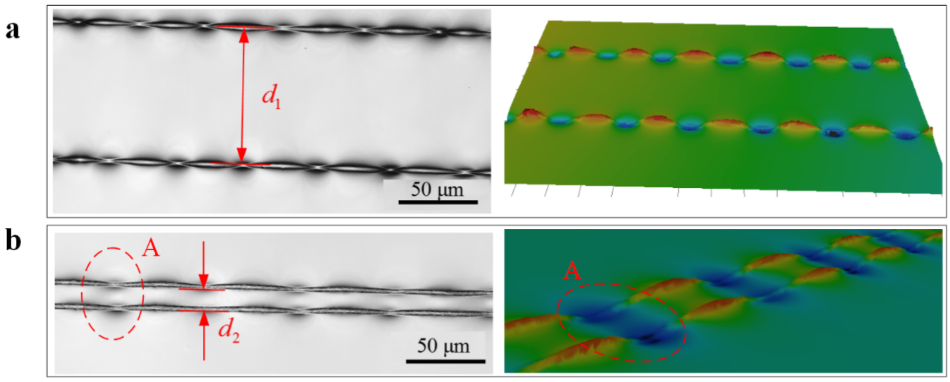

Figure S8. The influence of spacing to the conformance of out-of-surface buckling. The right columns are the 3D views of the left columns.

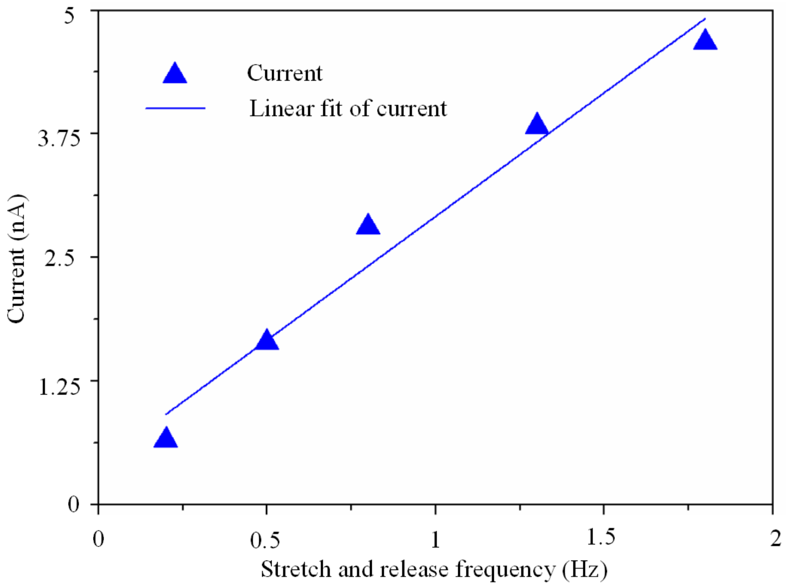

Figure S9. The output current of device consisting of 40 fibers with respect to stretch and release frequency. The applied strain is 70%.

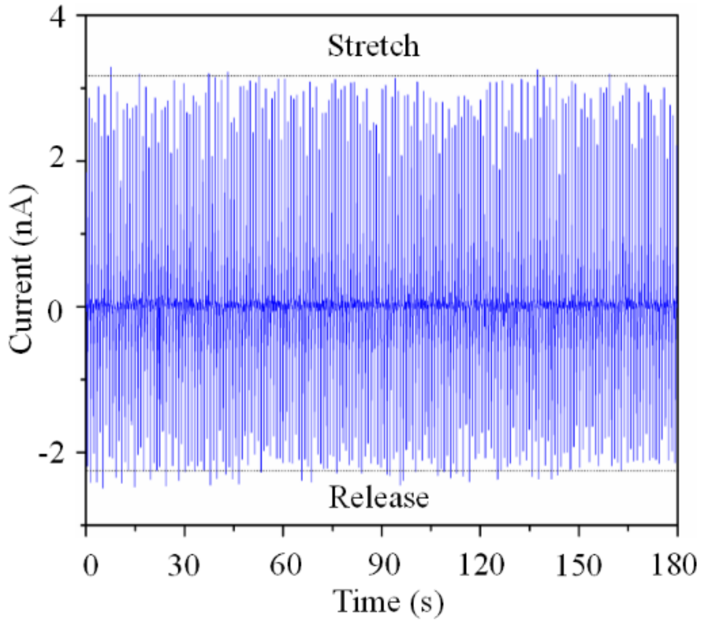

Figure S10. Reliability test of device consisting of 40 PVDF fibers under an applied strain of 100%.

The total energies of in-/normal-to-surface buckling

For a given fiber-on-substrate system, whether in-surface or normal-to-surface buckling happen, the total energy consists of three parts, including the bending energy U_{b1}, U_{b2} (Subscript 1 means normal-to-surface buckling, subscript 2 means in-surface buckling) due to fiber buckling, membrane energy U_{m1}, U_{m2} in the fibers, and substrate energy U_{s1}, U_{s2} in the substrates.

For a specific fiber-on-substrate system, among all the material and geometry parameters, only the moment of inertia in normal-to-/in-surface directions (I_1, I_2) are different. Let $E_f I_1$, $E_f I_2$ denote the normal-to-surface and in-surface bending stiffness of the electrospun fiber, $E_f A$ denotes the tension stiffness of the fiber. On the basis of work of previous researchers and our experiment, the deflection of the fiber is almost sinusoidal, so the in-/normal-to-surface deflection can be described as $V_1 = V_{m1}\cos k_1 x$, $V_2 = V_{m2}\cos k_2 x$, where $k_1 = 2\pi/\lambda_1$, $k_2 = 2\pi/\lambda_2$, λ_1, λ_2 are the wavelength of the buckling system.

For the normal-to-surface buckling system, the bending and membrane energy per unit length of the buckled fiber are[1]

$$U_{b1} = \frac{k_1}{2\pi}\int_0^{\frac{2\pi}{k_1}} \frac{1}{2} E_f I_1 [\frac{\partial^2 V_1}{\partial x^2}]^2 dx = \frac{E_f I_1}{4} k_1^4 V_{m1}^2 \tag{1}$$

$$U_{m1} = \frac{1}{2} E_f A \varepsilon_{m1}^2 = \frac{1}{2} E_f A [\frac{1}{4} V_{m1}^2 k_1^2 - \varepsilon_{pre}]^2 \tag{2}$$

Where ε_{m1} denotes the membrane strain of the fiber, ε_{pre} denotes the prestrain of the substrate.

The strain energy per unit length in the substrate is

$$U_{s1} = \frac{k_1}{2\pi}\int_V \sigma_{ij}\varepsilon_{ij} dV = \frac{P_1^2}{4\pi \bar{E}_S}(3 - 2\gamma - 2\ln\frac{k_1 W}{2}) \tag{3}$$

where $P_1 = -E_f A V_{m1} k_1^2 (k_1^2 V_{m1}^2 / 4 - \varepsilon_{pre}) - E_f I_1 V_{m1} k_1^4$, $\gamma = 0.577$ is the Euler's constant, W is the contact width between fiber and substrate. $\bar{E}_s = E_s/(1-\nu_s^2)$, E_s and ν_s are the elastic modulus and Poission's ratio of the substrate.

The total energy in the fiber-substrate can be obtained as

$$\begin{aligned} U_{tot1} &= U_{b1} + U_{m1} + U_{s1} - \frac{1}{\lambda_1}\int_0^{\lambda_1} P_1 \cos k_1 x (V_1 - V_{m1}\cos k_1 x)dx \\ &= \frac{E_f I_1}{4} k_1^4 V_{m1}^2 + \frac{1}{2} E_f A \left(\varepsilon_{pre} - \frac{1}{4} V_{m1}^2 k_1^2\right)^2 - \frac{P_1^2}{4\pi \bar{E}_S}\left(3 - 2\gamma - 2\ln\frac{k_1 W}{2}\right) \end{aligned} \tag{4}$$

The minimization of the total energy U_{tot1} with respect to V_{m1} and k_1 gives the equations of V_{m1} and k_1, then the total energy U_{tot1} can be simplified as

$$\bar{U}_{tot1} = \frac{1}{2} E_f A \varepsilon_{c1}(\varepsilon_{pre} - \varepsilon_{c1}) \tag{5}$$

where $\varepsilon_{c1} \approx \sqrt{\frac{\bar{E}_S}{E_f}} \times \frac{\sqrt{I_1}}{A}\left(\frac{9}{16} + 16\pi/9/(3 - 2\gamma - 2\ln\frac{3}{4} - \frac{1}{2}\ln\frac{W^4}{16}\frac{\bar{E}_S}{E_f I_1})\right)$ is the critical buckling strain, or the minimum strain needed to induce buckling. When $\varepsilon_{pre} \le \varepsilon_{c1}$, the fiber only compress, and when $\varepsilon_{pre} > \varepsilon_{c1}$, the fiber buckles normal-to-surface.

For in-surface buckling system[2], the bending and membrane energy per unit length of the buckled fiber is similar to normal-to-surface, where $U_{b2} = \frac{E_f I_2}{4} k_2^4 V_{m2}^2$, $U_{m2} = \frac{1}{2} E_f A [\frac{1}{4} V_{m2}^2 k_2^2 - \varepsilon_{pre}]^2$. The strain energy per unit length in the substrate is a little different that $U_{s2} = \frac{P_2^2}{4\pi\bar{E}_S}(\frac{3-\nu_s}{1-\nu_s} - 2\gamma - 2\ln\frac{k_2 W}{2})$, where $P_2 = -E_f A V_{m2} k_2^2 (k_2^2 V_{m2}^2/4 - \varepsilon_{pre}) - E_f I_2 V_{m2} k_2^4$.

The total potential energy of the in-surface system is

$$U_{tot2} = \frac{E_f I_2}{4} k_2^4 V_{m2}^2 + \frac{1}{2} E_f A \left(\varepsilon_{pre} - \frac{1}{4} V_{m2}^2 k_2^2\right)^2 - \frac{P_2^2}{4\pi\bar{E}_S}\left(\frac{3-\nu_s}{1-\nu_s} - 2\gamma - 2\ln\frac{k_1 W}{2}\right)$$

, which can also be simplified as $\bar{U}_{tot2} = \frac{1}{2} E_f A \varepsilon_{c2}(\varepsilon_{pre} - \varepsilon_{c2})$, where $\varepsilon_{c2} \approx \sqrt{\frac{\bar{E}_S}{E_f}} \times \frac{\sqrt{I_2}}{A}\left(\frac{1}{2} + 2\pi/(5 - 2\gamma - 2\ln\frac{5}{7} - \frac{1}{2}\ln\frac{W^4}{16}\frac{\bar{E}_S}{E_f I_2})\right)$ is the critical buckling strain for in-surface buckling, it's the same meaning with ε_{c1}.

When comparing the two total energies, U_{tot1} and U_{tot2}, we can get that the buckling mode with a smaller critical buckling strain has a smaller total energy, that is, energetically favorable. The critical buckling strain is related to both the material properties ($\overline{E}_s / E_f$) and cross-section of the fibers (I_1, I_2, A, W). For a fiber on substrate, parameters like $\overline{E}_s / E_f$, A and W are independent of direction, so the moment of inertia of the fibers (I_1, I_2) in different directions are key to determining the buckling modes.

Calculation of the critical buckling strain for an isosceles trapezoid section

The section of the fiber is complex, but it can be simplified as an isosceles trapezoid with an interior angle of $67°$. The inertia in in-surface/normal-to- surface direction is $I_{insurface} = \frac{1}{12}W^3H - \frac{1}{2}kH^2[\frac{1}{72}k^2H^2 + (\frac{1}{2}W - \frac{1}{6}kH)^2]$, $I_{normal} = \frac{H^3(6W^2 - 6kWH + k^2H^2)}{36(2W - kH)}$, where $k = 2/\tan 67^\circ$.

The critical strain of these two buckling modes can be converted to

$$\varepsilon_{c\_normal} = \sqrt{\frac{\bar{E}_s}{E_f}} \times \frac{2\sqrt{m}}{x(2-kx)} \times (\frac{9}{16} + \frac{16}{9}\frac{\pi}{3 - 2\gamma - 2\ln\frac{3}{4} - \frac{1}{2}\ln\frac{\bar{E}_s}{E_f} + \frac{1}{2}\ln(16\times m)} \tag{6}$$

$$\varepsilon_{c\_insurface} = \sqrt{\frac{\bar{E}_s}{E_f}} \times \frac{2\sqrt{n}}{x(2-kx)} \times (\frac{1}{2} + \frac{2\pi}{5 - 2\gamma - 2\ln\frac{5}{7} - \frac{1}{2}\ln\frac{\bar{E}_s}{E_f} + \frac{1}{2}\ln(16\times n)} \tag{7}$$

where $x = H/W$, $m = \frac{x^3(6 - 6kx + k^2x^2)}{36(2-kx)}$, $n = \frac{1}{12}x - \frac{1}{2}kx^2[\frac{1}{72}k^2x^2 + (\frac{1}{2} - \frac{1}{6}kx)^2]$.

Let the elastic ratio of substrate to fiber $\bar{E}_s / E_f$ and the height to width ratio H/W be the coordinates, the critical strain for the trapezoid section is showed in Figure S5a.

For sections like rectangular and semi-elliptical (Figure S6), the calculation of critical strain is similar to the calculation process above.

Calculation of the critical buckling strain for section having equal bending stiffness in in-/normal-to-surface directions

For cross-section which has equal bending stiffness in in-/normal-to-surface directions, such as circular、square、regular octagon etc., the critical strain can be converted to

$$\varepsilon_{c\_normal} = \frac{A}{W^2}\sqrt{\frac{\bar{E}_S}{E_f}}\sqrt{\frac{I}{W^4}}\left(\frac{9}{16}+\frac{16}{9}\frac{\pi}{3-2\gamma-2\ln\frac{3}{4}+2ln2-\frac{1}{2}\ln\frac{\bar{E}_S}{E_f}+\frac{1}{2}ln\frac{I}{W^4}}\right) \quad (8)$$

$$\varepsilon_{c\_insurface} = \frac{A}{W^2}\sqrt{\frac{\bar{E}_S}{E_f}}\sqrt{\frac{I}{W^4}}\left(\frac{1}{2}+\frac{2\pi}{5-2\gamma-2\ln\frac{5}{7}+2ln2-\frac{1}{2}\ln\frac{\bar{E}_S}{E_f}+\frac{1}{2}ln\frac{I}{W^4}}\right) \quad (9)$$

The corresponding critical strain for both in-surface and normal-to-surface is shown in Figure S7. The coordinate $\sqrt{I/W^4}$ is a dimensionless number, and each number repensents a specific section, such as square section corresponds $1/\sqrt{12}$, Regular Hexagonal section corresponds $5\sqrt{3}/16$. Figure S7a shows that for cross-section which has equal bending stiffness, in-surface buckling mode always has lower critical strain, that is, energetically favorable. Figure S7b is an example of $\bar{E}_S/E_f=1.9\times10^{-5}$ ($E_s=2$ Mpa, E_f=140Gpa), the result is consistent with Ryu's experiment[3] that silicon nanowires (SiNWs) which has regular hexagonal cross-section buckle only within the substrate surface.

References

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2 J. Xiao, S. Y. Ryu, Y. Huang, K. C. Hwang, U. Paik and J. A. Rogers, *Nanotechnology*, 2010, **21**, 085708.
3 S. Y. Ryu, J. L. Xiao, W. Il Park, K. S. Son, Y. Y. Huang, U. Paik and J. A. Rogers, *Nano Lett.*, 2009, **9**, 3214-3219.