ESI Guide

Electronic Supplementary Information for

Bioinspired wet-assembly fibers: from nanofragments to microhumps on string in mist

Cheng Song[1], Lin Zhao[1], Wenbo Zhou[1], Minhui Zhang[1], Yongmei Zheng[*1]

Supporting Information

This file contains：

Mechanism and optimizing of fragment-on-string fibers

Supplementary Figures S1-S3

Supplementary Analysis S1-S5

---

[1] School of Chemistry and Environment, Beijing University of Aeronautics and Astronautics, Beijing, 100191, P. R. China.

[*] Correspondence and requests for materials should be addressed to Y. Z. (zhengym@buaa.edu.cn)

Mechanism and optimizing of fragment-on-string fibers

After collected by a shelf connected with the cathode (**Figure S1a**), the micro PVDF fiber can form a unique fragment-on-string structure, different from those commonly collected on the foil (Figure S1b-c), which may be owing to the remaining DMF on the foil, dissolving the fragments caught by the fiber. Those nanofragments may be produced during the electrospinning process and then caught by the hanging PVDF fibers which act as the fibrous filtration[1-4] because the fragments and humps are both composed of PVDF (**Figure S2**) and their spreading density on the fiber (V_p/V_f, V_p, V_f represent the total volume of the fragments and the fiber holding them) is almost linear dependent on the delay time of the shelf in the electrospinning chamber after the electrospinning ends (**Figure S3a**). Moreover, the density also has an obvious S-shaped relationship with the concentration of PVDF (**Figure S3b**), as the PVDF can completely dissolve in DMF (N,N-dimethylformamide) in low concentration, leaving no fragments electrospun and caught by the fiber while when the solution is too dense, the undissolved PVDF is still in large pieces, which cannot be electrospun either, which make the value of V_p/V_f increased slow in extremely low and high concentration, but sharp in the middle part. Thus, we chose PVDF concentration of 11 wt% and delay time of 12 h as the optimal results.

Figure S1：

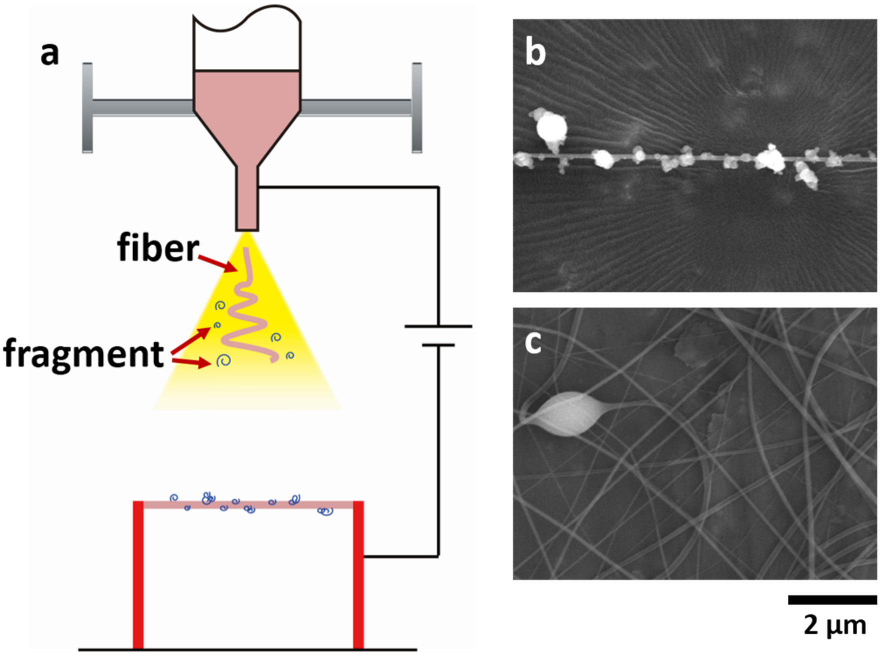


Figure S1. a, Illustration of the improved electrospun facilities. The spinnable PVDF solution is fed through a movable needle via a soft tube. When a high voltage is applied, an electro hydrodynamic approach is carried out. The electronspun fiber with nanofragments is formed via static delay time. The fibers on the shelf can catch the nanofragments (b) while those on the foil still remain smooth (c), due to the slow evaporating of DMF on the foil.

Figure S2：

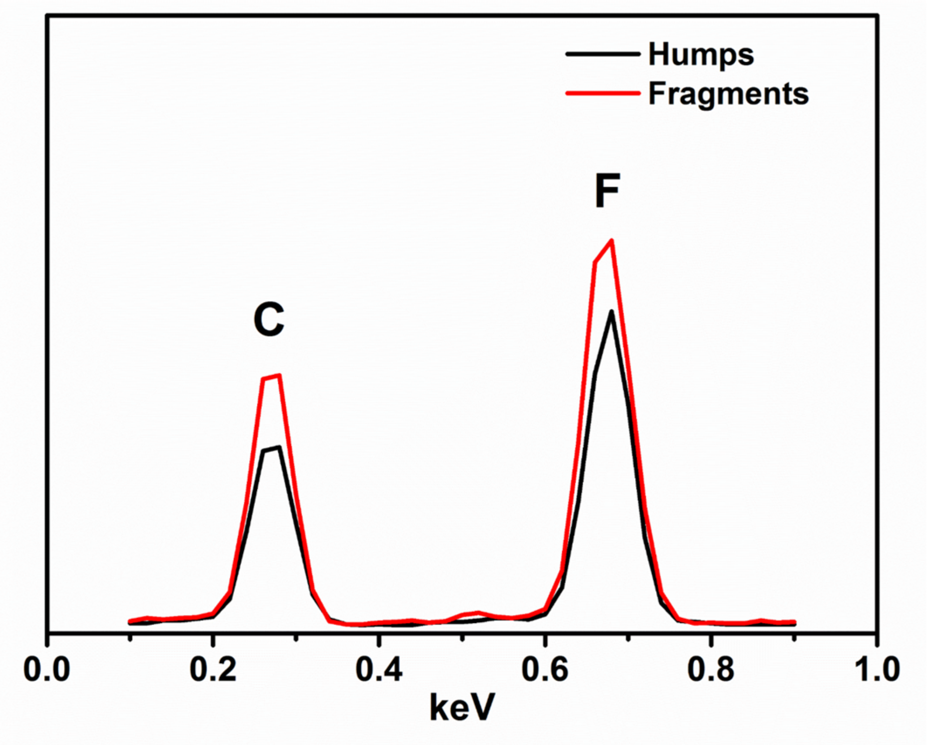


Figure S2. EDS results of nanofragments (red) and microhumps (black). The elements were identified as carbon (C) and fluorine (F), which can also originate from the PVDF structure. A semi-quantitative relationship of the chemical elements can be calculated based on the their peak sizes in the spectrum. The results of humps and nanofragments we observed was ~0.57 and ~0.58, respectively, which were quite near the theoretical one excluding errors and impurity of PVDF (~0.63).

Figure S3;

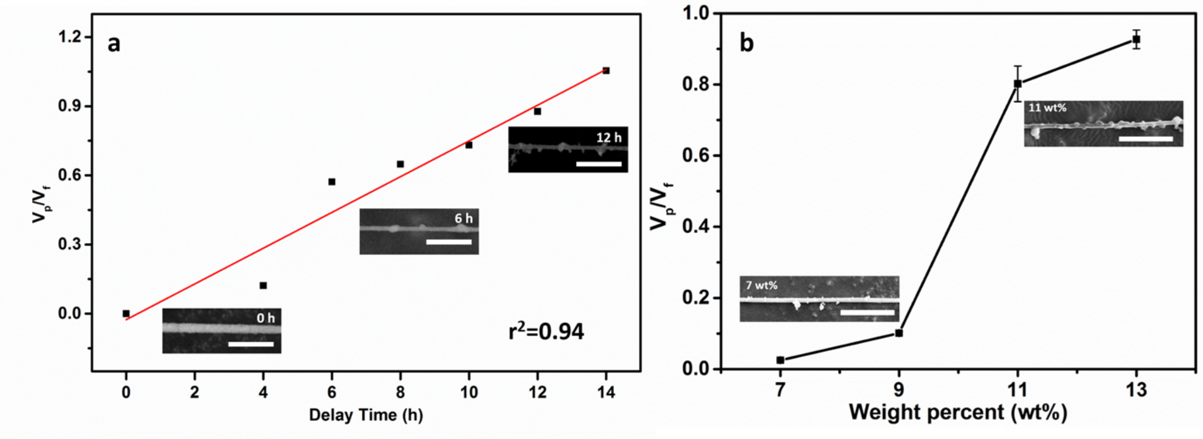


Figure S3. The relationship between density of fragments on the fiber with delay time and PVDF concentration. The density has a linear growth with the delay time continuing (a) while an S-shaped relationship with the PVDF concentration. Scale bar: 2 μm.

Figure S4

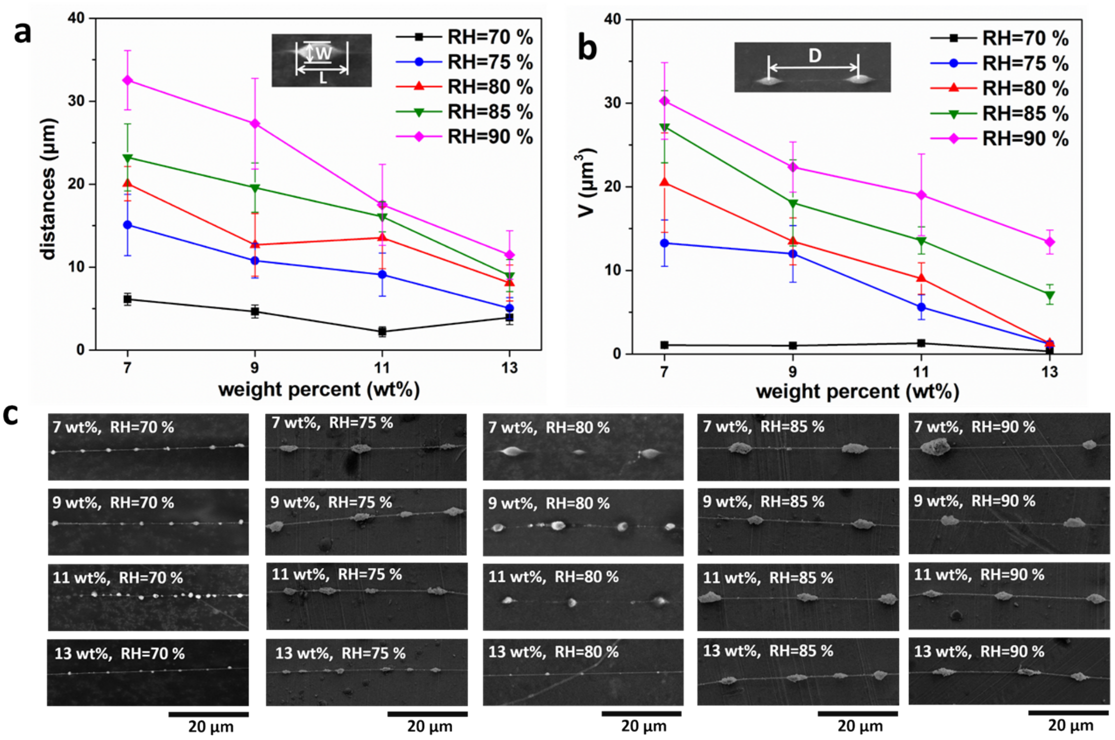


Figure S4. The average distance between the humps and hump volumes in different PVDF concentration and RH. a, b) Relationship of hump distances and hump volumes of different PVDF concentration at different RH. With the increase of PVDF concentration, both distances (a) and hump volumes decrease. c) SEM images of the self-assembled microhumps of different PVDF concentration (7 wt%, 9 wt%, 11 wt% and 13 wt%) when RH=70 %, 75 %, 80 %, 85 % and 90 % (wet-assembly time=30 s).

References

1 H.-S. Park and Y. Park, *Korean J. Chem. Eng.* , 2005, **22**, 165-172.

2 R. Sahay, P. S. Kumar, R. Sridhar, J. Sundaramurthy, J. Venugopal, S. G. Mhaisalkar and S. Ramakrishna, *J. Mater. Chem.* , 2012, **22**, 12953-12971.

3 J. Schaeffer and L. Olson, *Filtr. Sep.* , 1998, **35**, 124-129.

4 K. M. Yun, C. J. Hogan Jr, Y. Matsubayashi, M. Kawabe, F. Iskandar and K. Okuyama, *Chem. Eng. Sci.* , 2007, **62**, 4751-4759.

Analysis S1:

If we note Re and Pe as Reynolds number[1] and Péclet number[2] of the stream, respectively, then we have:

$$\mathrm{Re} = \frac{\rho v_0 d_f}{\mu} \tag{I-1}$$

and

$$\mathrm{Pe} = \frac{v_0 d_f}{D} \tag{I-2}$$

where ρ, v_0, μ are the mean density, mean velocity and intrinsic viscosity of the stream,respectively; d_f, D are the diameter of the fiber and the diffusion coefficient which can be given by Stokes-Einstein equation[3,4]:

$$D = \frac{k_B T C_u}{3\pi\mu d_p} \tag{I-3}$$

where k_{B}, T, d_p are the Boltzmann constant, absolute temperature and diameter of the particles, respectively, and C_u is Cunningham slip correction factor[5] due to the small diameter of the particles, which, under normal pressure and temperature, can be written as:

$$C_u = 1 + \frac{2\lambda}{d_p}[1.257 + 0.4\,exp(-1.1\frac{d_p}{2\lambda})] \tag{I-4}$$

where λ is the mean free path of gas molecules (λ=0.066 μm).

In our experiment, T =293 K, v_0=0.1 m/s, if we assume $d_f \approx$ 200 nm, $d_p \approx$ 1 μm (the diameter of water drops produced by our ultrasonic nebulizer are in the range of 0.5 ~ 5 μm) and the steam is saturated steam, whose intrinsic viscosity is 9.727×10^{-6} Pa·s^{-1} , then we can easily get $C_u \approx 1.166$ and $D \approx 5.174\times10^{-11}$ m^2·s^{-1}. According to Eq. (I-1) and (I-2), we will have $\mathrm{Pe} \approx 400 >> 1$ and $\mathrm{Re} \approx 4\times10^{-11} < 1$.

References

1. Reynolds, O. An experimental investigation of the circumstances which determine whether the motion of water shall be direct or sinuous, and of the law of resistance in parallel channels. *Proc. R. Soc. London* **35**, 84-99 (1883).
2. Squires, T. M. & Quake, S. R. Microfluidics: Fluid physics at the nanoliter scale. *Rev. Mod. Phys.* **77**, 977-1026 (2005).
3. Einstein, A. Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen. *Annalen der Physik* **322**, 549-560 (1905)
4. Cussler, E. L. *Diffusion: Mass Transfer in Fluid Systems*. (Cambridge University Press, 1997).
5. Cunningham, E. On the Velocity of Steady Fall of Spherical Particles through Fluid Medium. *Proc. R. Soc. London, Ser. A* **83**, 357-365 (1910)

Analysis S2:

In the range of Pe>>1 and Re<1, η_{f} can be calculated through Langmuir's equoiton[1]:

$$\eta_{\mathrm{f}} = \frac{1}{2\mathrm{La}}\left(2x\ln x - x + \frac{1}{x}\right)$$

$$\mathrm{La} = 2 - \ln \mathrm{Re}$$

$$x = 1 + 1.308\left(\frac{\mathrm{La}}{\mathrm{Pe}}\right)^{\frac{1}{3}} \qquad \text{(II-1)}$$

which can be simplified into

$$\eta_{\mathrm{f}} = 1.75\frac{1}{\mathrm{La}^{\frac{1}{3}}}\mathrm{Pe}^{-\frac{2}{3}} = 1.75\left[2 - \ln\left(\frac{\rho v_0 d_f}{\mu}\right)\right]^{-\frac{1}{3}}\left(\frac{v_0 d_f}{D}\right)^{-\frac{2}{3}} \qquad \text{(II-2)}$$

As ρ, v_0, μ and D are all gas constant which are irrelevant to d_f, Eq. (II-2) can be seen as a function of d_f:

(II-3)

$$\eta_f = f(d_f) = C(-3.18 - ln\, d_f)^{-1/3} d_f^{-2/3}$$

As the order of magnitude of df is about 10^{-7} (a ew hundred nanometers), we can get

$$\eta_{\mathrm{f}} \approx C_0 \cdot d_f^{-\frac{2}{3}} > 0 \qquad \text{(II-4)}$$

References:

1. Langmuir, I. & Suits, C. G. *The Collected Works of Irving Langmuir: Atmospheric phenomena*. (Published with the editorial assistance of the General Electric Company by Pergamon Press, 1961).

Analysis S3:

According to Young's law, we can first define the coalescence-induced difference of the surface energy (ΔE_c) as1:

$$\Delta E_c = \gamma_{LV} \Delta A_{LV} - \gamma_{LV} \Delta A_{SL} \cos\theta \qquad \text{(III-1)}$$

where γ_{LV}, ΔA_{LV}, ΔA_{SL}, θ is the surface energy of liquid-vapor interface, the changes of liquid-vapor and solid-liquid surface areas, and the Young's contact angle, respectively. We assume that the larger drop (with the radius of R_0) were made from two smaller ones of the same size (both with the radius of r_0), due to the mass conservation principle, R_0 and r_0 have a relationship :

$$2 \times \frac{4}{3} \pi r_0^3 = \frac{4}{3} \pi R_0^3$$

$$R_0 = 2^{\frac{1}{3}} r_0 \qquad \text{(III-2)}$$

Then Eq. (III-1) will be written as:

$$\begin{aligned} \Delta E_c &= \gamma_{LV} \left(4\pi R_0^2 - 2 \times 4\pi r_0^2 \right) - \gamma_{LV} \cos\theta \frac{\pi d_f^2}{4} \left(4r_0 - 2R_0 \right) \\ &= -\pi \gamma_{LV} \left(1.65 r_0^2 + 0.37 r_0 d_f^2 \cos\theta \right) \\ &\approx -1.65 \pi \gamma_{LV} r_0^2 < 0 \qquad (\text{as } r_0 >> d_f) \end{aligned} \qquad \text{(III-3)}$$

References:

1. Boreyko, J. B. & Chen, C.-H. Self-Propelled Dropwise Condensate on Superhydrophobic Surfaces. *Phys. Rev. Lett*. **103**, 184501 (2009)

Analysis S4:

The capillary adhesion for a larger hanging-drop on a rough-curve fiber (f_c) can be described as[1,2]:

$$f_c = r \cdot 4\pi b\gamma \sin\alpha \qquad \text{(V-1)}$$

where r is the roughness, α is off-axis angle ($\sin\alpha = 1 - h/R$, h is the height of drop above the fiber, R is the radius of drop), γ is the surface tension of water, b can be calculated by averaging the number of drop covering the beads and the spacing of beads, which is:

$$b \sim \frac{kb_r + nb_a}{k+n} \qquad \text{(V-2)}$$

where k and n were the number of 'knots' and of spacing between 'knots' covered by drop, respectively; and b_r, b_a are the maximum and minimum radii of silk with periodic knots, respectively.

In our experiment, as the largest drop hung on one segment of fiber between two beads, we have k=2, n=1, $b_r = R_{\text{beads}} \approx 2.16$ μm (Fig. 3b) and $b_a = R_{\text{fiber}} \approx 0.30$ μm (Fig. 3b and Fig. S2b). According to Eq. (V-2), b is 1.54 μm.

As the surface tension (f_c) should be balanced by the gravity, we then have:

$$r \cdot 4\pi b\gamma \sin\alpha = 4\pi\rho_w g R^3 / 3$$

$$r = \rho_w g R^3 / 3b\gamma \sin\alpha \qquad \text{(V-3)}$$

Given $\sin\alpha \approx 1$ (as h can be ignored relative to R), r can be estimated roughly to ~ 7.98, larger than that of the natural spider silk[1].

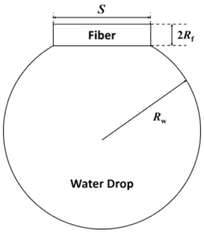
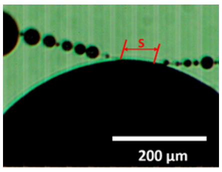
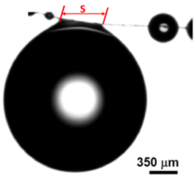
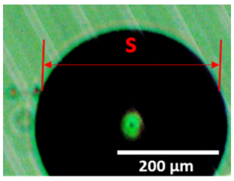
References:

1. Huang, Z., Chen, Y., Zheng, Y. & Jiang, L. Capillary adhesion of wetted cribellate spider capture silks for larger pearly hanging-drops. *Soft Matter* **7**, 9468-9473 (2011).
2. Wenzel, R. N. Resistance of solid surfaces to wetting by water. *Ind. Eng. Chem.* **28**, 988-994 (1936)

Analysis S5:

BWMF may collect a larger drop, which the volume (V_{drop}) of drop can be estimaed as following **table S1**, and some parameters can be defined: L is the wet-contact length of the fiber; R_f , R_w is the radius of the fiber and the drop, respectively. Thus $V_{fiber}=\pi L R_f^2$, and $V_{drop}=4\pi R_w^3/3$, where V_{fiber} is volume of fiber in wet-contact.

Table S1 Estimation of the collected drop volume and compare of volumes

	Illustration	BWMF	Spider silk[1]	Dip-coating fiber[2]	Smooth PVDF fiber
					
S (μm)		80	519	1130	338
R_f (μm)		0.30	6.5	15	0.30
R_w (μm)		650	950	1400	185
V_{drop} (μm^3)	$4\pi R_w^3/3$	1.15×10^9	3.59×10^9	1.14×10^{10}	2.65×10^7
V_{fiber} (μm^3)	$\pi S R_f^2$	22.6	6.89×10^4	7.99×10^5	95.6
V_{drop}/V_{fiber}		5.09×10^7	5.21×10^4	1.43×10^4	2.77×10^5

Note: S is wet contact length between fiber and drop.

References:

1. Huang, Z., Chen, Y., Zheng, Y. & Jiang, L. Capillary adhesion of wetted cribellate spider capture silks for larger pearly hanging-drops. *Soft Matter* **7**, 9468-9473 (2011).
2. Bai, H., Ju, J., Zheng, Y. & Jiang, L. Functional Fibers with Unique Wettability Inspired by Spider Silks. *Adv. Mater.* **24**, 2786-2791 (2012).