Supporting Information

Excellent bead-on-string silkworm silk for drop capturing ability

Yuan Chen, Jia He, Lin Wang, Yan Xue, Yongmei Zheng* and Lei Jiang

The supplementary information including:

Supplementary experimental methods

Measurement on velocity of removing the PVDF coated silk fiber;
Experiment of phase separation;
Measurement of stress and strain of fiber;
Control on non-formation of Rayleigh instability;
Measurement of hanging-drop volume;

Supplementary analysis

Calculation of adhesion on BBS and NSS and estimation on maximum volume of hanging-drop

Supplementary figure legends

Fig. S1-8
Supplementary Experimental Methods:

*Measurement on velocity of removing the PVDF coated silk fiber:* The silkworm silk is fixed on the U-shaped bracket, and the U-shaped bracket is fixed on a dip-coater machine. The fiber is drawn out horizontally by the dip-coater machine with accurate velocities.

*Experiment of phase separation:* The phase separation experiment is done in a Polycarbonate (PC) sealed transparent box. The box has two holes for humidifier and sensor to detect temperature and humidity. The phase separation is completed in the environment of relative humidity of 70% at temperature of 20°C.

*Measurement of stress and strain of fiber:* The dynamic contact angle measuring instrument (DCAT11, Data-Physics, Germany) is the standard instrument for the weight based measurement of surface and interfacial tension with high precision ranging from 10 μg to 210 g (namely 0.98 μN to 2.058 N). Because the stress of single silkworm silk is very small. We choose one silk with 15 mm, one side vertically fixed on the movable bottom of DCAT and the other fixed on the bracket linked to electronic balance. The bottom moves with the silk and the computer program records the weight measured by balance with movement distance ∆L. The stress force can be calculated by $F = mg$, which $m$ is the weight and $g$ is the gravitational constant. $F_{(Stress)} = m_{(breaking point)} g$ and Strain=$\Delta L/L$. 50 samples are repeated to get the average value.

*Control on non-formation of Rayleigh instability:* We get a uniform PVDF silk without Rayleigh instability in a very low concentration (0.5%) and a low velocity (10 mm/min) based on our fabrication condition (see Fig. S3). Due to low concentration, the solution film on the fiber is too thin to break up. In a typical fiber coating method, the coating film thickness is affected by capillary number $Ca = \eta V/\gamma$, where the $\eta$ is the solution viscosity, $V$ is the drawing velocity and $\gamma$
is the solution surface tension. The lower velocity is, the less Ca is. And these two reason leads to the Rayleigh instability hard to observe.

*Calculation on periodicity of beads:* The periodicity of beads is calculated using software by measuring the centre distance of two beads. According to the length of two spindle-knots with L=lD, where l is the coefficient and D is the diameter of fiber, the periodicity of spindle-knots is determined by the thickness of solution film on the fiber, which is changed with the concentration and drawing-out velocity. The BBSs are fabricated by 9% PVDF/DMF solution and 50 and 150 mm/min drawing-out velocity (10 samples each velocity). We choose the spindle-knots with given height (H) of ~ 119±10 µm and periodicity (L) increasing from 750 to 1050 µm. And we further choose the spindle-knots with given periodicity (L) of ~ 1058±58 µm and height (H) ranging from 115 to 185 µm. I have added the errors.

*Estimation of drop volume:* The large drop is considered as the ellipsoid shape. The whole volume is calculated with \( V = 4\pi r_a^2 r_b / 3 \), where \( r_a \) is the semi-minor axis; \( r_b \) is the semi-major axis. The \( r_a \) and \( r_b \) can be measured by a photograph measure software.
Supplementary analysis

Calculation of adhesion on BBS and NSS and estimation on maximum volume of hanging-drop:

Bioinspired fibers with micro- and nanoscale roughness of the PVDF coating have more capillary adhesion than uniform fibers\(^1\). If a drop is pending from a uniform fiber, the gravity (\(G=4\pi \rho g R^3/3\)) of the drop can be balanced with the surface tension \(\pi \gamma D\), where the \(\gamma\) is the surface tension \(D\) is the diameter of fiber. According to the model of drops hanging on uniform fiber\(^2\), the force is equivalent by two similar fibers connected radially to the drop at the same location, and the total of capillary force is \(4\pi b_0 \gamma \sin(\alpha + \beta)\), where \(\alpha\) is the off-axis angle, \(b_0\) is the radius of fiber, \(\beta\) is the true receding angle. But for a rough curved spindle-knots, it is more complex. Considering the roughness, the surface adhesion is enhanced according to Wenzel’s law\(^3\). So the capillary force is increasing due to the roughness introduced. The capillary force is \(f=r \cdot 4\pi b_0 \gamma \sin(\alpha + \beta)\), where the \(r\) is the roughness, the \(b\) is the effective radius of fiber\(^1-4\). As for NSS, capillary force for a hanging-drop can be estimated with \(f_{NSS} = r \cdot 4\pi b \gamma \sin \beta\), \(\alpha=0\). We estimated the volume of the drop hanging on the NNS \(\sim 0.8\) \(\mu\)L at \(b=0.02\) \(\mu\)m and \(\beta=23^\circ\). It can be theoretically estimated that the strong hanging-drop force for the volume of hanging-drop is 4.6 times more than that of NSS. But as for a curvature geometry with bead-on-string on fiber, the effect of the Laplace pressure difference is further considered to play a role. The capillary adhesion for a larger hanging-drop can be described as: \(f_{BBS} = r \cdot 4\pi b \gamma \sin(\alpha + \beta) + \Delta_{Laplace} \) (\(\gg f_{NSS}, \beta_B \sim \alpha + \beta\)), where \(\Delta_{Laplace} = A \cdot b \gamma \sin(\alpha + \beta)\), (\(A=0.4652\); on bead-on-string fiber, \(b\) can be estimated with, \(b=(kb_r+nb_a)/(k+n)\), where \(k\) and \(n\) are the number of ‘beads’ and of spacing between ‘beads’ covered by drop, respectively; \(b_r\) and \(b_a\) indicated the maximum and minimum radii of fiber with periodic beads. According to the equation \(f_{BBS}\), given \(r \sim 1.12\) (\(r\) is...
roughly estimated according the experimental values in Fig. 2), the theoretical values (corresponding points in Fig. 4) can be estimated (see Table S1-2).

References:

2. E. Lorenceau, C. Clanet and D. J. Quere, *J. Colloid Interface Sci.*, 2004, 279, 192. (ref. 22)

**Table S1** Compare on volumes of hanging-drops with the same height (~119 ± 10 µm)

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<th>b/µm</th>
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<th>β/°</th>
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**Table S2** Compare on volumes of hanging-drops with the same periodicity (~1058 ± 58 µm)

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Supplementary Figure Legends (Fig. S1-8):

**Fig. S1** SEM images of silkworm silk. **a)** Surface of silkworm silk and **b)** two exposed main silks in silkworm by observation with low magnification. **c)** The exposed main silk with diameter of ~ 9 μm, respectively, and silkworm silk with diameter of ~ 20 μm. Scale bars, (a,b) 100 μm; (c) 10 μm.
**Fig. S2** Optical image (a) and SEM image (c) of natural silkworm silk (NSS) with diameter of ~20 μm. A optical image (b) and SEM image (d) bioinspired of bead-on-string silkworm silk fiber (BBS) that composed of the rough PVDF geometric beads surrounding the main-axis of silkworm silk, similar to the spindle-knots and joints of wetted spider silk of *cribellate* spider. Scale bars, (a,b) 400 μm; (c,d) 200 μm.
**Fig. S3** Optical images (a) and statistical of the height (b) and width (c) of the controllable fabrication of bioinspired bead-on-string silk (BBS). The different geometries can be fabricated on silkworm silk when the concentrations of PVDF in DMF are range from 1%, 3%, 5%, 7% to 9% (in weight) and drawing-out velocity ranged from 10, 50, 100, 150, to 200 mm/min. The height and width of spindle-knots are obvious increasing with the concentration. But it is not a line relationship between height (or width) and velocity. The height and width of spindle-knots are obvious increasing with the concentration. At the low concentration, as for example for 1% and 3% concentrations, lower viscosity makes no enough PVDF solution to form a film on the silkworm silk. But it isn’t the more, the better. If the concentration is too high (>10%), the film dries before it can break up into droplets. The spindle-knots are always asymmetric in shape or can’t well connect along the silk (shown in Fig. S5). However, the velocity factor is more complex. In our experiment, too low or too high velocities are both not good for spindle-knot droplet formation. We choose the optimal velocity to fabricate the BBS, for example 100–150 mm/min. So we can select the different periodicity and size of beads to study the property of hanging-drop in solid-liquid interfaces. Scale bar, (a) 200 μm.
**Fig. S4** SEM images of bead on BBS. **a-d)** The gradual magnified images of bead, where the rough curvature structures can be observed on the spindle bead (**c,d)**. Scale bars, (a) 100 µm; (b,c,d) 10 µm.
Fig. S5 SEM images of bead-on-string formation on silkworm silk and on nylon fiber and structural formula of PVDF and amino acids. The same concentration of PVDF in DMF is 10% (in weight). a-b) The bead-on-string on silkworm silk. The bead (height ~110 μm, width ~252 μm) is excellent connecting to the string along the silkworm. c-d) Bead (height ~115 μm, width ~250 μm) and string on nylon fiber. The bead-on-string isn’t well connected along silk under the same concentration above for the same ages. Scales bars, (a,c) 200 μm; (b,d) 50 μm. e) PVDF structural formula and f) amino acids structural formula. It is known that the surface of PVDF is composed of -CH₂-CF₂- groups, which would be hydrophobic, while the surface of silkworm silk is composed of amino acids, like glycine, alanine and L-serine, which contain a lot number of hydrophilic groups. Usually, a hydrophilic surface would favour the water collection. The physical interaction makes easy to form hydrogen bonds with –NH₂-, -OH and –CO- groups of amino acids. It may be the reason that silkworm silk has better attachment with PVDF than nylon fiber. Nylon fiber is composed of a lot of –CH₂- groups. It only produces weak van der Waals force with PVDF. And the -CH₂-segment portion has greater degree of molecular chain curl, which makes the binding force weaker.
Fig. S6 The shortened three-phase contact line on curved bead-on-string. When the fiber is tilted to the critical angle (a), the contact angle at bead-on-string is decreasing to the receding contact angle (b). The solid-liquid-gas three-phase contact line begins to slide from the bead-on-string, which leads to the decrease of the contact line length between fiber and water drop. It also greatly reduces the solid-liquid adhesion force. Water drop is easily detached off from curved bead-on-string because of gravity.
**Fig. S7 Illustration on estimation of larger water-condensed drop in volume.** The larger drop is regarded as the ellipsoid shape. Given the $V$ is the whole volume, $r_a$ is the semi-minor axis, $r_b$ is the semi-major axis, the whole volume ($V$) of drop: $4\pi r_a^2 r_b/3$. 
Fig. S8  a-b) SEM image of silkworm silk and uniform PVDF silkworm silk. c-d) Water capturing on silkworm silk and uniform PVDF silkworm silk. The two drops show the similar cases on silkworm silk and on uniform PVDF silkworm silk. Scales bars, (a, b) 20 μm; (c, d) 500 μm.