Nanoscale

MINIREVIEW

Check for updates

Cite this: Nanoscale, 2019, 11, 15448

Hierarchical fibers for water collection inspired by spider silk

ponents. Based on this characteristic, numerous bioinspired fibers have been fabricated for water collection. Herein, we review the water-collection process for spider silk and recent vital advances in bioinspired fibriform materials, focusing on the water-collection mechanisms of spindle-knot fibers, which exhibit directional droplet transport, hanging mechanism and hanging ability. Also, we evaluated their water-col-

lection abilities on a micro- and macro-scale, which gave a better view for the design of bioinspired

water-collection materials. These advances enable the significant use of bioinspired fibers in water collec-

tion, which may be applied in several other fields, such as directional transport, tissue engineering, oil-

Received 13th May 2019, Accepted 19th July 2019 DOI: 10.1039/c9nr04065j

rsc.li/nanoscale

1. Introduction

Freshwater scarcity is regarded as a global systemic risk and two-thirds of the global population suffer from water shortage.

^aMinistry of Education Key Laboratory for the Green Preparation and Application of Functional Materials, Hubei University, Wuhan 430062, People's Republic of China. E-mail: zguo@licp.cas.cn; Fax: +86-931-8277088; Tel: +86-931-4968105 ^bState Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China For arid areas, this issue may even put an entire country in an extremely vulnerable position.^{1,2} Water, as the indispensable element for organisms, has become an increasing demand to meet all aspects of human society, including daily use, irrigation and industry.³ As one of the available water resources, fog has drawn increasing attention in the water-collection field, especially in arid and hemi-arid zones. Fog collection is a modern method for acquiring freshwater, which has been studied for its feasibility and sustainability.^{4,5} This technology is simple and energy-saving, but has the disadvantages of

Mr W biomin (BMT) in 20 degree intere. wettak tional wettak

Wei Chen

Mr Wei Chen joined Prof. Guo's biomimetic materials of tribology (BMT) group at Hubei University in 2018 to pursue his PhD degree. His current scientific interests are focused on surface wettability and designing functional materials with special wettability.

water separation and biosensors.



Zhiguang Guo

Feb 2009 to Feb 2010, he worked in the Department of Physics, University of Oxford, UK, as a visiting scholar. Currently, he is a full professor in LICP financed by "Top Hundred Talents" program of CAS. To date, he has published more than 250 papers about the interfaces of materials.

Water scarcity plagues two-thirds of the global population. Interestingly, researchers have found that spider silk exhibits excellent water-collection ability owing to its unique structure and chemical com-

ROYAL SOCIET

View Article Online

Professor Zhiguang Guo received

his PhD from Lanzhou Institute

of Chemical Physics (LICP),

Chinese Academy of Sciences (CAS) in 2007. After that, he

joined Hubei University. From

Oct 2007 to Aug 2008, he worked

at the University of Namur

(FUNDP), Belgium, as a post-doctoral researcher. From Sep 2008 to Mar 2011, he worked at the Funds of National Research

Science (FNRS), Belgium, as a "Charge de Researcher". During being seasonal, localized and unsustainable.⁶ In regions that are foggy but have scarce water, it is possible to set up apparatus to effectively gather water since devices are becoming more advanced.^{7–11}

Due to the requirement of environmental adaptability, a handful of fauna and flora have evolved to adapt in arid environments, such as spider silk, cactus, and Namib beetle. One of the intriguing features of spider silk is its ability to collect water from humid air. When tiny water drops condense, the puff rebuilds its morphology to shrink into opaque bumps and ultimately forms periodic spindle-knots. As condensation continues, the droplets grow in size and move to the nearest spindle-knots.¹² Similarly, cacti collect water due to their unique spine with conical shape. Spine clusters and trichomes are distributed on the cactus surface, and each spine contains barbs and gradient grooves. These three parts play different roles in the process of fog collection, enabling fog water to deposit, grow, transfer and preserve.¹³ Namib beetles collect water from humid wind on their back, which has alternating hydrophobic and hydrophilic regions. The water deposited on their back can coalesce onto their hydrophilic peak, and each droplet grows to reach a critical size. When the size of the droplets crosses a critical value, the capillary force of the attached area is overcome and the droplets detach and roll down the back of the beetle and move to its mouth.¹⁴ Besides these two, many other examples have been explored, including Bermuda grass,¹⁵ Syntrichia caninervis,¹⁶ Cotula fallax,¹⁷ Salsola crassa,¹⁸ Eremopyrum orientable¹⁹ in the past few years.²⁰ These organisms are endowed with distinct features, which help them adapt to arid environments.

Based on these unique natural organisms, researchers have developed numerous bioinspired materials to address the current water shortage conundrum. Our group has been devoted to the field of water collection, exploring the mechanisms of water-collection and creating intelligent materials with efficient water-collection ability.²¹⁻²⁵ Herein, we review how spider silk possesses a special mechanism for water condensation, transport and coalescence, demonstrating that bioinspired microfibers have wide application prospect. We focus on the water-collection mechanisms of spindle-knot microfibers, and evaluate their water-collection abilities on a microscopic and macroscopic scale. This review will help to understand the ingenious structure of microfibers and design of novel materials to address water scarcity. Moreover, the design of bioinspired microfibers can be extended to other in fields such as tissue engineering,²⁶ oil-water separation²⁷ and biosensors.28

2. Water collection on spider silk

Spider silk is characterized by its diverse chemistry, structure and functions. This extraordinary material has prompted researchers to explore their potential applications owning to their excellent mechanical strength and structural properties.^{29–32} Some spiders can spin multiple high performance fibers, which contain high strength dragline silk and elastic silk.³³ The phenomenon of water collection on spider silk can be seen everywhere, and the drops tend to coalesce on the intersections.

The secret of water harvesting on spider silk has been revealed, where the water-collection phenomenon emerged evidently in cribellate spider silk. Differently from the ecribellate spider, the cribellate spider has cribellum made of many spigots, which can extrude a bunch of nanofibers. Cribellate spiders can spin two types of fibers, pseudoflagelliform silk and periodic puffs made of cribellate nanofibrils.^{34,35} Researchers have studied the water-collection ability of the cribellate spider Uloborus walckenaerius, and explored the watercollection mechanisms of the spider silk.^{12,36,37} As shown in Fig. 1a, the spider silk is made of two main-axis fibers and regular puffs. When the dry spider silk is placed in a fog atmosphere, the silk transforms its shape to become slender, which is shown in Fig. 1b. Water coating plasticizes the silk and endows additional elasticity from the surface tension of the liquid.^{38,39} The spider silk achieves wet-rebuilding and its structure is totally reversible.⁴⁰ The wetting process is shown in Fig. 1c-h.¹² As tiny water droplets condense on the silk, the puffs shrink gradually and finally transform into spindleknots. Interestingly, as condensation continues, the water droplets ceaselessly grow and are directionally transported toward the spindle-knots. Then these drops start to coalesce with each other and eventually form bigger drops. As illustrated in



Fig. 1 (a) Low-magnification environmental SEM image of periodic puffs and the joints surrounding two main-axis fibers. (b) Environmental SEM images of periodic spindle-knots linking slender joints. The apex angle of the spindle-knots (2β) is about 19°. (c) Dry spider silk with four semitransparent puffs. In mist, a few tiny water drops (indicated by arrows) first condense on the puffs. (d–f) Puffs shrink to opaque bumps with water condensing and form spindle-knots linked by joints. (f–h) Directional water collection on the wet-rebuilt multi-structural spider silk. (i) Spindle-knot is randomly interweaved by nanofibrils. (j) Image of a joint, which is composed of nanofibrils aligned relatively parallel to the silk axis.¹² (Copyright 2010, Nature).

Minireview

Fig. 1h, the drops hang on one spindle-knot and double spindle-knots.

To understand the water drop transport to the spindle knots, images of the spindle-knot and joint were taken, as shown in Fig. 1i and j, respectively.¹² The image of spindleknot presents random nanofibers with a rough surface morphology, which induces a high surface energy. In contrast, the image of the joint shows that the nanofibers are arranged orderly with an axial arrangement, which endows the surface with low surface energy. Hence, the surface morphology creates a surface energy gradient along the joint to the spindle-knot. This gradient drives the water droplet to move towards a more wettable region with a high surface energy. In addition, another force gives rise to spontaneous water transport, which comes from the conical shape of the spindle-knot. The conical geometry creates a difference in Laplace pressure. The drop on the conical-shaped spindle-knot reduces the surface and moves to a low surface energy. Then the drop is transported from the joint with a large curvature to the spindle-knot with a small curvature. Therefore, the driving forces originate from the surface energy gradient and difference in Laplace pressure, which can induce water droplet transport from the joint to the spindle-knot.

3. The approaches for bioinspired fibers

3.1 Electrodynamic method

Electrospinning is a special fiber manufacturing process for more than 50 types of polymers, including biopolymers, watersoluble polymers, organosoluble polymers, and molten polymers.⁴¹ The fiber diameter ranges from tens of nanometers to hundreds of micrometers. The ultrathin structure mainly depends on the working mechanism of electrospinning. A schematic illustration of the electrospinning setup is shown in Fig. 2a.⁴² The polymer solution in a syringe is fed through the spinneret at a controllable rate under the action of a pump. As the high voltage discharges, the drop at the nozzle is electrified and distorted in a conical shape, which is known as a Taylor cone. When the strength of the electric field crosses a threshold value, the electrostatic force overcomes the surface tension, resulting in liquid ejection from the nozzle. The liquid jet undergoes a stretching process under the sustained electrostatic force and forms an ultrathin and continuous fiber after the solvent evaporates.

In previous research, PEO fibers with beads were obtained *via* electrospinning and the mechanism for the formation of the beads was revealed.^{43,44} The solution viscosity, jet, net charge density and surface tension of solution are the main factors that affect the morphology of the fibers. The thinner the fibers, the closer the distance between the beads and the smaller the diameter of the beads. A higher viscosity tended to form fibers without beads and a higher net charge density helped to form thinner fibers. The formation of the beads was ascribed to the surface tension driving the liquid film to break



Fig. 2 (a) Schematic illustration of the basic setup for electrospinning. The insets show a drawing of the electrified Taylor cone and a typical SEM image of the nonwoven mat of poly(vinyl pyrrolidone) (PVP) nanofibers deposited on the collector.⁴² (Copyright 2004, Wiley-VCH). (b) Schematic illustration of the setup and process for the preparation of necklace-like chains.⁴⁶ (Copyright 2010, American Chemical Society). (c) Illustration of the formation of the humped-fiber. The nanofragments on the fiber condense water drops, which subsequently coalesce and self-assemble into microhumps on the fiber.⁴⁹ (Copyright 2014, Royal Society of Chemistry). (d) Illustration of combined electrospinning and electrospraying approaches.⁵¹ (Copyright 2011, Wiley-VCH).

up, thereby an increase in surface tension favors the formation of beads. Rayleigh instability involves fluid breaking up into tiny droplets with a lower surface area. By using the Rayleigh instability principle, bead-shaped microfibers with varying compositions and structural properties can be designed.⁴⁵

However, in the research on spindle-knot microfibers, electrospinning has become a major technique combining electrospray, wet-assembly, coaxial electrospinning. A one-step method to prepare necklace-like structures *via* electrospinning was achieved.^{46–48} Poly(vinyl alcohol) (PVA) is suitable as polymer matrix due to its hydrophilicity and excellent mechanical properties. As shown in Fig. 2b, a PVA solution containing SiO₂ nanoparticles was extruded by a DC high-voltage generator and formed necklace-like fibers. The nanoparticles with relatively small diameters aggregated into clusters, and the large nanoparticles tended to regularly align one by one. The necklace-like fibers were relatively easy to fabricate and suitable for the application of water collection. Although the fibers were prepared with regular beaded structures, the fiber surface with one polymer matrix may hamper dropwise transport.

As a different method to fabricate spindle-knots, nanofragments/nanoparticles were applied to fabricate beads *via* the wet-assembly method, which exhibited a good performance. Microhump fibers were successfully fabricated *via* electrospinning and water coalescence-induced self-assembly

methods.⁴⁹ A PVDF solution was fed through a movable needle and pumped out by the electrospinning equipment. Then the as-produced fibers were fixed away from the foil to capture fragments, which were also produced during the electrospinning process. As illustrated in Fig. 2c, when the fibers with nanofragments were put into a continuous steam, tiny water drops started to condense to cover the fragments on the microfibers. With condensation continuing, the tiny drops grew in size and coalesced with each other. Hence, coalescence drove the fragments to assemble into clusters. The clusters were small and close initially, but became larger and dispersed at the end. When the steam was cut off and the water evaporated completely, humps were formed along the fibers. Similarly, titanium tetrachloride (TiCl₄)-hydrolyzed particles were also be applied for the fabrication of beads via wet-assembly.⁵⁰ When PMMA fiber was exposed to smoke containing modified Ti nanoparticles, these particles arbitrarily deposited around the fibers. Then the fibers were transferred in a humid atmosphere and the wet-assembly phenomenon occurred. After dehydration treatment, beads containing the Ti nanoparticles were distributed on the fiber.

Coaxial electrospinning is a versatile method for multiple applications, which has been used for the fabrication of spindle-knot fibers. The coaxial electrospinning method is a combination technique, in which the inner fluid is wrapped by sheath flow. As shown in Fig. 2d, two metallic needles are fixed coaxially to produce two fluids in the same direction.⁵¹ The dynamic mechanism is the same as conventional electrospinning, which caused by a high-voltage generator. The inner fluid with high viscosity and outer fluid with low viscosity are initially extruded and combined. Poly(ethylene glycol) (PEG) solution as the outer fluid and polystyrene (PS) solution as the inner fluid form a suitable combination. The inner polymer with a low surface-free energy can mitigate the viscous drag force, and the outer polymer with a higher surface-free energy tends to break up and transform into a spindle-knot shape. However, the limitation of PEG is that it water-soluble and could swell and shrink in different humidity; thus, the sustainability of PEG fibers is largely reduced. Hence, poly(methyl methacrylate) (PMMA) is used as an outer fluid for the formation of beads.⁵² The morphology of the fibers can be regulated by tuning the flow rate and concentration of the inner and outer fluids. When the flow rate of the outer fluid is 3.0 mL h⁻¹ and the corresponding flow rate of the inner fluid is 0.5 mL h⁻¹, regular beads appear. Poly(N-isopropylacrylamide) (PNIPAM) is also used to fabricate beads due to its hydrophilic nature.⁵³ The PVDF is chosen as a core fluid due to its hydrophobic feature and mechanical stability. Additionally, a cross-linker is added to enhance its stability at hydrophobic-hydrophilic interface. The alternating regions on the fibers create a surface energy gradient, which promotes water drop transport.

Co-electrospinning can be used to construct a liquid core encapsulated in polymer fibers. Differently from the bilayer melting phase, the liquid core is hardly shaped on the spinneret. An approach was proposed to encapsulate a liquid core in solid fibers, which resulted in beaded microfibers, and a hydrophobic fluid was efficiently encapsulated inside the beads.^{54,55} A low oil/melt interfacial tension value and high viscosity of the outer fluid are vital to shape and maintain the compound cone in a steady state. In contrast, for high interfacial tension and low viscosity, the viscous drag force exerted by the melt is unable to overcome the cohesive force of the surface tension, causing the oil meniscus to remain quasispherical, and no oil separates from the meniscus. The outer liquid was poly(vinyl pyrrolidone) (PVP) and inner liquid was oil, with the flow rates of 0.4 and 0.04 mL h⁻¹, respectively. Under these conditions, both the compound cone and emitted current appeared in the steady state.

In a study on the macroscopic patterns of electrospun fibers, nanoimprint lithography applied to fiber meshes aimed to create physically deformed patterns, which could result in multiple physical properties.⁵⁶ The fibers were modified by the transfer of promising topographies. The surface wettability and structure could be regulated. Thus, abundant possibilities for spatially controlling surface properties can be envisioned.

3.2 Dip-coating method

Widely used in coating, the dip-coating method has attracted a significant interest in the fabrication of spindle-knot fibers. Its method and mechanism are relatively facile and simple compared with other methods. A schematic illustration of the dipcoating method is shown in Fig. 3a.⁵⁷ Before the immersion process, both a regular fiber and polymer solution are prepared as precursors. Then the fibers are immersed in the polymer solution and horizontally drawn from the tank after a period of time. The drawing velocity can be tuned to acquire a moderate polymer solution by a machine. Hence, the fiber will be coated by a cylindrical polymer film. Immediately, the polymer film breaks up and transfers into tiny drops attached around the fibers due to Rayleigh instability. After the solvent evaporates, the tiny drops are solidified and form a spindleknot shape. Specifically, this method is to fabricate heterostructured fibers by imprinting another polymer matrix on the uniform fibers, spontaneously converting them into spindleknot fibers.

Understanding the factors affecting the geometric morphology is vital to fabricate promising spindle-knot fibers. The drawing velocity, concentration/viscosity and surface tension of the polymer solution are crucial to achieve periodic spindleknots with different sizes.⁵⁸ A series of fibers was fabricated to explore the relationship between the spindle-knot morphology versus different concentrations of polymer solution and drawing-out velocities. The optical images of the obtained fibers are shown in Fig. 3b. For a low concentration, there was not enough solution to draw out around the fiber to induce Rayleigh break-up, causing the thin polymer film to be stable on the surface.59 In this case, high velocity was critical to allow the solution to detach from the reservoir and induce the appearance of drops. However, for the highly viscous solution, the polymer film was thick and hardly broke up into drops, causing the fiber surface to dry before the appearance of



Fig. 3 (a) Scheme for the fabrication of bioinspired fibers with a hump structure. A nylon fiber was soaked in a PMMA solution in DMF at an appropriate concentration.⁵⁷ (Copyright 2011, Wiley-VCH). (b) Optical images of BASs fabricated under different conditions by drawing the nylon fibers out of the PMMA/DMF solution. Statistical data for the (c) width and (d) height of the spindle-knots on the BASs fabricated under different solution concentrations (5%, 6%, and 7%) and drawing velocities (100, 125, 150, 175, and 200 mm min⁻¹).⁵⁸ (Copyright 2011, Wiley-VCH). (e) SEM images of the polymer bead-on-string fibers fabricated after different reaction times. Scale bar is 10 μ m. (f) SEM images of porous polymer beads fabricated under different RHs. Scale bar is 10 μ m.⁶² (Copyright 2013, Royal Society of Chemistry).

drops. In a given formula, the film thickness is decided by the capillary number (C_a), which can be presented as: $C_a = \eta V/\gamma$.⁶⁰ Although the solution viscosity (η) and drawing velocity (V) are positive in the coating process, surface tension (γ) may slightly decrease the C_a value because the change in surface tension is insensitive, while the viscosity increases significantly. Moreover, the size of the spindle-knots varies with the solution concentration and drawing velocity. At a constant velocity, both the height and width increase with the solution concentration, but the size changes irregularly with the velocity at a given concentration. As shown in Fig. 3c and d, the size significantly increased initially and then decreased with the drawing velocity. Hence, a suitable spindle-knot fiber can be fabricated by adjusting these three parameters.

Further, bioinspired fibers with different topographies can be constructed, including rough and porous structures. Fibers with rough/smooth spindle-knots were fabricated by tuning the solvent ratio in the reservoir and drying atmosphere.⁶¹ A series of fibers with different porous morphologies was fabricated by controlling the reaction degree of the polymer solution.⁶² As shown in Fig. 3e, fibers with smooth, less and homogeneous porous, and gradient porous and dented microstructures were obtained as the time for the polymer reaction increased. A porous structure makes the fiber surface more wettable, which is similar to that of wet spider silk. When the fibers are drawn from the reservoir and placed in humid atmosphere, water drops will deposit on the spindle-knot surface. After evaporation and solidification, the porous morphology is imprinted on the surface. Fig. 3f exhibits the spindle-knots with a smooth, homogeneous porous, wavy footprint morphology at incremental relative humidity.

The dip-coating method is suitable to coat diverse polymers on uniform fibers, which aims to construct spindle-knot fibers with a heterogeneous structure. For example, a series of raw fibers was immersed in four polymer solutions to fabricate different fibers with both smooth and rough knots.⁶¹ Fibers with rough PMMA knots were prepared by immersing nylon fibers in a PMMA/(DMF + ethanol) solution with a weight ratio of 7 : 100 : 1, in which the ethanol was conducive to construct a rough surface by drawing it out at a velocity of 200 mm s⁻¹. The fibers with rough PMMA knots were placed in a DMF atmosphere at 50 °C for 2 h, which converted the rough surface into a smooth surface. Similarly, poly(vinyl acetate) (PVAc), polystyrene (PS), and poly(vinylidene fluoride) (PVDF) could also be coated on the knots.

Based on the Rayleigh instability, the polymer film could be divided into multi-level spindle-knots. The bioinspired fibers with a hierarchical structure induced continuous gradients of surface-free energy and Laplace pressure differences.⁶³ As shown in Fig. 4a, a uniform nylon fiber was drawn out from a PVDF solution and the polymer film immediately broke into



Fig. 4 (a) Optical images of fabrication processes of bio-inspired spindle-knotted fiber obtained by high-speed CCD camera.⁶³ (b) Scheme for the fabrication of bio-inspired fibers with multi-gradient and multi-scale spindle knots. A carbon fiber was soaked in a PVDF–DMF solution.⁶⁴ (Copyright 2012, Royal Society of Chemistry). (c) Optical images showing that the cylindrical PVDF film breaks into gradient polymer droplets beginning from top to bottom.⁶⁶ (Copyright 2013, Nature). (d) Optical microscopy images of the spindle knots on the fiber surface with different stretching ratios.⁶⁷ (Copyright 2015, Wiley-VCH).

multi-size drops, coating the fiber. After the drying process, spindle-knots were formed coaxially. The main spindle-knots had a height of 75 µm and width of 200 µm. Second-level spindle-knots were formed between the large knots and thirdlevel spindle-knots formed around the bigger knots. Similarly, the template method was also suitable for fabricating fibers with multi-gradient and multi-scale spindle-knots.⁶⁴ As shown in Fig. 4b, after first forming the spindle-knots, the as-prepared fiber was then immersed in epoxy resin solution and drawn out. The resin polymer was both coated on the spindleknots and formed smaller spindle-knots on the smooth regions. The satellite spindle-knots exhibited excellent ability to coalesce drops, and their shape was conducive to prolonging the three-phase contact lines, which enhanced their ability to hang a bigger drop. The same method was applied to coat graphene on the surface of spindle-knots.⁶⁵ The multilayered graphene structure could induce a change in wettability upon laser etching, arising from the increased roughness extent. To obtain fibers with multi-gradient and multi-scale spindleknots, carbon fibers with PDMS spindle-knots were immersed in the graphene oxide solution and drawn out at a certain rate. After chemical reduction, the reduced graphene was successfully coated on the fiber surface. The directional motion of water drops could be regulated effectively by controlling the wettability of graphene surface.

Similar to multi-level spindle-knots, a bioinspired fiber with gradient spindle-knots was prepared by the tilt dipcoating method.⁶⁶ The fiber was drawn out from the reservoir at a tilt angle to a horizontal line. As shown in Fig. 4c, the polymer film was coated with a gradient thickness due to gravity and then broke up into gradient drops. Further, these drops transformed into spindle-knots with their size decreasing gradually. Nevertheless, for water collection with these gradient spindle-knots, water drops tended to coalesce towards the bigger spindle-knots, which was attributed to the release of energy liberation, achieving directional movement in a long distance.

Elastic nylon fibers are commonly adopted as raw materials to fabricate bioinspired fibers via the dip-coating method. Their water-hanging ability and water-collection ability were discussed via dynamic regulation.67 In the same way, elastic bioinspired fibers were prepared by immersing a nylon fiber in a polydimethylsiloxane (PDMS) solution. The fibers could be stretched by applying certain tensile force. The optical images of the elastic fibers with different stretching ratios are shown in Fig. 4d. When the stretching ratio changed from 0% to 180%, the height, length and periodicity of the spindle-knot were transformed from 90 to 75 µm, 240 µm to 500 µm, and 510 to 1380 µm, respectively. The elastic fiber could moderate the water-collection ability by exerting a large tension, which resulted from the change in the three-phase contact line. Compared with nylon fibers, an enhanced water-collection performance was presented using raw silkworm silk.⁶⁸ The hydrophilic fibroin of the silkworm silk combined well with the biocompatibility of PVDF, and thus the spindle-knots were more strongly imprinted on the silkworm silk. In addition, the

mechanical properties of bioinspired silkworm silk are much better than that of natural silkworm silk, which prevented the contact line from decreasing. Hence, the bioinspired spindleknots could hang bigger water drops.

3.3 Microfluidic method

The microfluidic fabrication method via a microfluidic platform has been considered as a new tool to create continuous microscale polymeric structures in small quantities. A hydrodynamic fabrication technique using a microfluidic device was introduced to create continuous alginate fibers.^{69,70} The apparatus is fabricated by incorporating a glass pipette into a preformed hole in a PDMS substrate, as shown in Fig. 5a. The photopolymerizable sample fluid and non-polymerizable sheath fluid are introduced into the two input ports and combined at the outlet of the inner pipette. A coaxial sheath flow around the sample flow is formed at the staggered position of both flows. Using the same fabrication principle, microtubes and multilayer microfibers can be fabricated using similar apparatus, as shown in Fig. 5b. The core fluid, sample fluid and sheath fluid are individually introduced to produce a core/ sample/sheath flow construct. Afterwards, a microfluidic mode consisting of a digital, programmable flow control is introduced to continuously generate microfibers with regulable morphologies and chemical features, as shown in Fig. 5c.⁷¹ By switching the flow through a digital control scheme, a microfiber with different chemical compositions along its length can be obtained, which can even load gas bubbles, and live cells can be spatiotemporally coded. As shown in Fig. 5d, two alternating flows are controlled to generate microfibers with spaced spindle-knots. To mimic the porous structure of natural silk, a flow containing alginate solution and salt at a high flow rate is injected to construct spindle-knots. As shown in Fig. 5e, the porous structure is generated by salt dissolution and it creates a gradient surface energy for water transport.

Therefore, with preparation technology, microfluidics is versatile in many fields, such as oil absorption⁷² and cell culture.73-75 This method has been developed enormously. The fabrication of spindle-knots via microfluidics has been realized to be critical for the fabrication of bioinspired microfibers. As shown in Fig. 5f, a coaxial capillary microfluidic technique was developed for designing promising spindle-knot microfibers.⁷⁶ The inner alginate solution was spun and injected into a calcium-tagged middle pregel phase, which acted as a flow sheath to coat the spun microfiber. Diffusion of the calcium ions from the sheath fluid into the alginate fluid facilitated gelation. The sheath solution was then emulsified by an immiscible outer oil fluid, and consequently transformed into spindle-knots around the inner fiber, which could be polymerized by ultraviolet irradiation. Then a hetero-structured gel fiber was continuously formed at the fluid outlet. By employing the same co-flow method, a sheath fluid containing graphene oxide and N-isopropylacrylamide pregel solution was transformed into drops by ionic gelation and emulsification.⁷⁷ The near-infrared absorption of graphene oxide and thermally responsive shape transition of the N-isopropylacrylamide

uν

Open 🖵 Closed

loint

Wate



Fig. 5 (a) Basic apparatus for the fabrication of microfibers. (b) By adding an additional stage, the apparatus is capable of producing microtubes.⁶⁹ (Copyright 2004, Royal Society of Chemistry). (c) Conceptual description of the process of generating coded fibers. (d) Schematic of a digital control scheme for the generation of artificial spindle-knots and joints by means of topography modulation and nanoporous structure coding. (e) Schematic of a fiber with a different surface energy and water-collection mechanism.⁷¹ (Copyright 2011, Nature). (f) Capillary microfluidic system for the fabrication of spindle-knotted microfibers. The detailed images show the successive steps of microfiber joint spinning, fluid coating, and knot emulsification. (g) Real-time microscopic images of the microfluidic generation process of the spindle-knotted microfibers with tunable spacing and size of the spindle knots. The scale bar is 500 µm.⁷⁶ (Copyright 2016, Wiley-VCH).

endowed the gel fibers with photothermally responsive watercollection ability.

The form of the spindle knot formed via emulsification could be distinguished as two types, core liquid used as the knot and sheath liquid used as the knot. The oil core, emulsified by an immiscible continuous fluid, was wrapped by the outer fiber, which exhibited a homogeneous feature on the surface.78 However, when the sheath liquid was used as the knot, the generated fiber presented a heterogeneous feature on the surface.⁷⁶ The behavior of one immiscible fluid turning into another leads to the formation of drops arising from the break-up of Rayleigh instability. Surface tension and shear force interact with the flow, which causes the interruption of the flow and the shaping of the drops.^{79,80} The morphology of the microfibers obtained via microfluidics can be affected by the flow rate of both fluids, interfacial tension and even device geometry. As shown in Fig. 5g, the size and interval of the spindle knots are highly controllable by adjusting the flow rates of the streams.⁷⁶ Furthermore, these controllable performances favor the understanding of the relationship between water-collection ability and structure.

As a natural linear polysaccharide, alginate has been widely employed in the fabrication of microfibers, especially exhibiting the property of gelation in the microfluidic method. Alginate solution can spontaneously solidify via the addition of Ca²⁺ ions, and thus alginate has an advantage as the

Nanoscale

polymer matrix in microfluidics.⁸¹ As shown in Fig. 6a, the preparation of calcium alginate fibers can be carried out using a coaxial microfluidic device.⁸² The liquid paraffin as the dispersed phase is injected into sodium alginate microflow. When the terminal of the fluid is in contact with the CaCl₂ solution, the effluent is instantly crosslinked to form calcium alginate fibers. In the formation of spindle-knots, the oil fluid is easily emulsified by the sheath fluid to form monodispersed drops because the oil-aqueous interfacial tension seeks to minimize the interfacial area due to the thermodynamic principle of minimum interfacial energy. Then a flexible microfiber with tunable magnetic spindle-knots for controlled 3D assembly is introduced.⁷⁸ The oil mixture containing magnetic Fe₃O₄ nanoparticles is injected in the alginate flow for the fabrication of bioinspired microfibers with magnetic spindle-knots, which is shown in Fig. 6b. After solvent evaporation and dehydration, the microfiber shape is converted into a spindleshaped microfiber. The microfibers can be properly manipulated for controllably moving, patterning and assembling under different magnetic fields, which creates opportunities for the fabrication of 3D scaffolds with complex network constructs.

The formation of spindle-knots is dependent on the heterogeneous core, which is coated on or dispersed in the continuous flow. Not only an oil core but also gas can be dispersed in aqueous solution for the fabrication of spindle-knots. A wellcontrolled bioinspired microfiber with cavity knots was fabricated via a gas-in-water microfluidic method.^{83,84} Differently from oil cores, the gas-in-water microfluidics adopts nitrogen or air as the dispersed phase to generate bubbles under the impact of the shear of the aqueous flow. The gas bubbles can be well-distributed in the alginate fiber, and the interval of bubbles can be controlled by the pressure of the gas phase. The surface morphology of the alginate microfiber is associated with the cavity-knot and joint, as exhibited in Fig. 6c and d, respectively. The cavity-knot is dehydrated faster than the joint part, which creates a gradient crack density with incremental surface energy, thus favoring water transport along the joint to the knot.

Cribellate spiders employ a simple one-step dry-spinning method to extrude two types of fibers. Multi-microchannels furnish a spinnable inner fluid and sticky outer fluid.³¹ Inspired by the natural spinning process, a bioinspired artificial microfiber by one-step dry-spinning method (a multi-



Fig. 6 (a) Schematic diagram of the experimental process for the preparation of fibers with spindle-knots.⁸² (Copyright 2015, Royal Society of Chemistry). (b) Schematic illustration of the microfluidic fabrication of calcium alginate microfibers with controllable magnetic spindle-knots.⁷⁸ (Copyright 2015, American Chemical Society). (c) SEM images showing the dehydrated cavity-microfiber. (d) SEM image showing the hollow cavity of the knot.⁸³ (Copyright 2017, Nature). (e) Multichannel microfluidic system (left) consisting of core flow and sheath flow, and the illustration on the right shows an enlarged biomimetic tapering channel. (f) Morphologies of fibers spun using regenerated silk fibroin solution as the core-spinning dope and silk sericin solution as the sheath-spinning dope.⁸⁵ (Copyright 2017, Wiley-VCH).

channel microfluidic chip) was invented.⁸⁵ In the microfluidic system, the microfluidic channel is divided into two wide straight channels and a gradually narrowing channel, as shown in Fig. 6e. An aqueous solution of regenerated silk fibroin is used as the core fluid in the main channel, while a silk sericin solution is used as the sheath flow in the outer channel. Since the flow rate of regenerated silk fibroin solution is equal to that of silk sericin, the composite fiber emerges with a core-sheath morphology. The surface morphologies of the core fiber and adhesive hemisphere are shown in Fig. 6f, presenting a fibrillar structure similar to natural silk, and the asymmetrical hemisphere appears on one side of the fiber due to the difference in both flow rates. The microfluidic method has great advantages in the fabrication of abundant fibers, and thus it is also deeply applied for the fabrication of spindle-knot microfibers. The generated microfibers are continuous, and the shape of the spindle-knot is facilely regulable.

3.4 Fluid-coating method

In contrast to the dip-coating method, the fluid-coating method has the advantage of continuity, which makes it possible to fabricate bioinspired microfibers on a large scale. A fluid-coating device is shown in Fig. 7a.⁸⁶ A nylon fiber is horizontally passed through a reservoir of PMMA solution and fixed in the capillary tube. The motor at the other end is used to drag the microfiber at an even velocity. The dynamic meniscus of the solution appears and wraps around the fiber when the motor opens. Then the polymer solution is detached from the reservoir and coated around the raw fibers. Immediately,



Fig. 7 (a) Schematic illustration of the fluid-coating method used for the large-scale fabrication of bioinspired fibers.⁸⁶ (Copyright 2011, Wiley-VCH). (b) Illustration of the unidirectional gradient-step spindleknots formed on a fiber. (c) Optical images of GSF with different gradient modes: unidirectional decreasing size; unidirectional increasing size; middle symmetric size; and two-side symmetric size, which were fabricated *via* the velocity-changeable drawing-out coating technique.⁸⁸ (Copyright 2014, Royal Society of Chemistry).

the liquid film is broken and assembled to form a polymer drop with a spindle-knot shape arising from Rayleigh instability. Then the solvent evaporates in such a short time that the long and continuous spindle-knot fiber can be collected directly.

In addition, the formation of the spindle-knots can be tuned by altering the solution parameters and the fiber-drawing velocities.^{86,87} When the drawing velocity is higher than the critical velocity, microfibers with periodic spindle-knots can be realized. At a drawing velocity below the critical velocity, the microfiber is uniformly coated with a thin polymer film. The critical velocity increases with a decrease in the solution concentration because more polymer solution is drawn out to aggregate into a thicker film when the motor velocity increases. The fluid-coating method is relatively facile, and the process is continuous. It is suitable for the preparation of large-scale and continuous bioinspired microfibers. Nevertheless, its stability and controllability need to be further study.

As mentioned above, similarly to the tilt dip-coating method, the fluid-coating method can achieve the spontaneous directional transport of water droplets over a long distance on the microfibers by changing the drawing velocity.⁸⁸ When the fiber is drawn from the polymer reservoir at a changing velocity with an acceleration at a limited distance, a conical film covers the uniform fiber, as shown in Fig. 7b. Then the liquid film immediately transforms into a convex–concave shape, subsequently becoming periodic polymer drops with a gradient height. Droplet-target transport can be modulated by fabricating gradient spindle-knots with various gradient modes, including middle and two-side symmetric gradient modes, which are shown in Fig. 7c. It is easier to realize droplet-target transport on fibers using the fluid-coating method.

4. Water collection mechanisms

4.1 Laplace pressure difference

For directional liquid transport, a water drop can be driven by shape, chemical and thermal gradients. Specifically, in the natural water collection process, water condenses on the silk and transports from the joint part to the spindle-knot part, which is shown in Fig. 8a. When the drop attaches on the fiber, the surface tension of water will generate Laplace pressure under the interface. If the shape of the droplet is not uniformly spherical, the Laplace pressure of each part of the surface will be very different. Therefore, there is discrepancy in the Laplace pressure on the spindle-knot and joint due to their different curvature radii. In various parts of the water drop, the Laplace pressure can be described as:

$$P_{\rm s} = \frac{2\gamma}{R}$$

where, γ is the surface tension of water and *R* is the curvature radius. At the two opposite sides of the drop, the Laplace pressure of the water drop on the joint is larger than that on the spindle-knot, which is due to the small curvature radius of



Fig. 8 (a) Mechanism of directional water collection on wet-rebuilt spider silk.¹² (Copyright 2010, Nature). (b) Stable TCL on artificial humped fiber during the growth of a hanging drop. High magnification image focusing on the solid/liquid contact region for the humped fiber. Scale bar, 200 μ m. Also shown is a sketch of the profile of the wetted region on the humped fiber from the side view. (c) Illustration of the "slope" effect and "curvature" effect.⁵⁷ (Copyright 2011, Wiley-VCH).

the surface on the side of joint and large curvature radius of the surface on the side of the spindle-knot. The asymmetric Laplace pressure causes the drop to transport to the side with a lower Laplace pressure. Hence, the conical shape will generate a pressure difference, which induces the water to move to the spindle-knot. The difference in Laplace pressure is described as follows:^{12,89}

$$\Delta P = -\int_{r_1}^{r_2} \frac{2\gamma}{\left(r+R_0\right)^2} \sin \alpha dz$$

where, *r* is the local radius, r_1 and r_2 are the radii of the knot at the two opposite sides of the drop, R_0 is the radius of the drop, α is the half-apex angle of the conical knot and dz is the integrated variable of the spindle-knot radius. Thus, the driving force exerted by the pressure difference will enable the water drop to achieve directional transport.

4.2 Surface-free energy gradient

The difference in Laplace pressure depends on the curvature gradient, while the surface-free energy difference depends on the composition or roughness gradient. The gradient of surface-free energy is another motivation to induce the droplet to move towards the more wettable region. The chemical composition and surface roughness are usually related to the wettability. A hydrophobic chemical composition corresponds to a hydrophobic surface with a low surface energy. In contrast, a hydrophilic chemical composition corresponds to a hydrophilic surface with a high surface energy. In the case of a hydrophilic fiber with a wettability gradient, the part with high surface roughness is more hydrophilic than the part with low surface roughness, and thus the part with high surface roughness has higher surface energy than the part with low surface roughness. Hence, an increase in surface roughness will generate a gradient surface energy. The surface wettability can be described by Wenzel's equation:

$$\cos\theta_{\rm w}=r\cos\theta$$

where, θ_w and θ are the apparent and intrinsic contact angles, respectively, and *r* is the roughness factor (r > 1), which is defined as the ratio of the actual area to the projected area on a rough surface. The roughness makes the hydrophilic surface more wettable and the hydrophobic surface less wettable. For hydrophilic spider silk, the joint is less rough and less hydrophilic, whereas the spindle knot is rougher and more hydrophilic. Specifically, the spindle-knot has a higher surface-free energy than the joint. The gradient surface-free energy along the joint to the knot generates a driving force, which is described as follows:^{12,90}

$$F = \int_{L_{
m j}}^{L_{
m k}} \gamma(\cos\, heta_{
m A} - \cos\, heta_{
m R}) {
m d}l$$

where, γ is the surface tension of water, θ_A and θ_R are the advancing and receding contact angles of the water drop on the spindle-knot, respectively, as shown in Fig. 8a, and dl is the integrating variable of the length along the joint (L_j) to the spindle-knot (L_k) . For natural spider silk, the gradient surface-free energy is produced by the gradient surface roughness, while the difference in the surface-free energy related to artificial silk can be achieved by altering the component. Hence, the roughness/component gradient contributes to driving the drop to move towards the spindle-knot.

4.3 Hysteresis resistance

Although the difference in Laplace pressure and the gradient surface-free energy are particularly remarkable in water drop motion, the hysteresis resistance always obstructs the movement of drops, especially in small drops with micrometer sizes. Since tiny drops coalesce with each other until their diameter exceeds the threshold size, the capillary force is predominant and the big drop begins to move.^{12,91} Hysteresis resistance is correspondingly obvious in wettable regions, and thus it is facile to drive the drop away from the joint, and a large hysteresis resistance makes it difficult to drive the drop away on the spindle-knot. In addition, the hysteresis resistance induces the drop to pin on the surface, causing the drop to move towards the spindle-knot when coalescence occurs.^{61,92}

4.4 Directional transport

For a water drop with a size less than the capillary length, the gravity is almost negligible. The directional transport can be ascribed to the cooperation of three main forces:^{61,93} (1) Laplace force due to the curvature gradient:

$$F_{\rm L} \approx \gamma_{\rm water} \left(\frac{1}{R'_{\rm J}} - \frac{1}{R'_{\rm K}}\right) \frac{\sin \alpha}{R_{\rm K} - R_{\rm J}} \frac{4}{3} \pi \left(\frac{R_0}{2}\right)^3$$
$$= \frac{\pi}{6} \gamma_{\rm water} \left(\frac{1}{R'_{\rm J}} - \frac{1}{R'_{\rm K}}\right) \frac{\sin \alpha}{R_{\rm K} - R_{\rm J}} R_0^3$$

where, γ is the surface tension of water, R_J and R_K are the local radii of the spindle-knot at the two opposite sides of the drop, corresponding to the curvature radii of the contact lines (R'_J and R'_K), respectively, α is the semi-apex angle of the conical shape, and R_0 is the radius of the coalesced bigger drop; (2) wetting force due to surface-free energy gradient:

$$F_{\rm W} \approx \pi R_0 \gamma_{\rm water} (\cos \theta_{\rm K} - \cos \theta_{\rm J})$$

where, $\theta_{\rm K}$ and $\theta_{\rm J}$ are the static contact angles at the spindleknot and joint, respectively; and (3) hysteresis force due to contact angle hysteresis:

$$F_{\rm H} \approx \pi R_0 \gamma_{\rm water} [(\cos \theta_{\rm rK} - \cos \theta_{\rm aK}) - (\cos \theta_{\rm rJ} - \cos \theta_{\rm aJ})]$$

where, θ_{rK} , θ_{aK} , θ_{rJ} and θ_{aJ} are the receding and advancing contact angles at the spindle-knot and joint, respectively. Consequently, for a hydrophilic spindle-knot, the total force of the water drop can be described as:

$$F_{\rm total} \sim F_{\rm L} + F_{\rm W} - F_{\rm H}$$

When $F_{\text{total}} > 0$, the drop is driven towards the knot, and when $F_{\text{total}} < 0$, the drop remains static. If the spindle-knot is less hydrophilic than the joint, the total force of the water can be expressed as:

$$F_{\rm total} \sim F_{\rm L} - F_{\rm W} - F_{\rm H}$$

In this case, if $F_{\text{total}} > 0$, the drop is driven towards the knot, but if $F_{\text{total}} < 0$, the drop is driven away from the knot. Thus, for natural and artificial silks, when the driving force arising from the Laplace pressure difference and surface-free energy gradient overcomes the maximal hysteresis force, the drop can move spontaneously.

4.5 Hanging mechanism

Large water drops can hang on thin fibers with knots more stable than that without knots, which is ascribed to the intense adhesion by the geometric feature of spindle-knots. In the collection process, the water drop tends to hang between two knots and grows to reach a critical size. As shown in Fig. 8b, the three-phase contact line (TCL) does not shrink apparently, and the total axial length of the contact region remains almost constant. The adhesion ability of the humps can be revealed by considering two distinct effects, the "slope" effect and "curvature" effect.⁵⁷ As shown in Fig. 8c, if the contact line attempts to contract from location "A" to "B" along the surface, the receding contact angle θ_r will decrease from $\theta_{r0} + \alpha$ to θ_{r0} , where θ_{r0} is the true receding angle and α is the semi-apex-angle of the hump. For a critical hanging drop, this process needs a large liquid surface distortion to activate the dewetting event. Thereby, the slope variation gives a higher barrier to inhibit the TCL from receding. If the contact line attempts to move from location "B" to "C", the curvature radius of the liquid at the solid/liquid interface will decrease from H/2 to D/2. The Laplace pressure will increase during this process due to the surface tension of the liquid, generating an energy threshold and the recession of the contact line is consequently hindered. The "slope" and "curvature" effects can

ensure the relative stability of the TCL and provide sufficient capillary force to hang a big drop water.

4.6 The length of the three-phase contact line

To evaluate the hanging ability of bioinspired fibers, the threephase contact line (TCL) is used to explore the water-collection behaviors and critical volume of a hanging water drop. When tiny water drops move toward the spindle-knot due to capillary force, they coalesce with each other to reach a big size and the water drop will transform into a hanging drop on the fiber. Under a continuous fog flow, the hanging drop is still growing. Meanwhile, the water drop needs to provide enough capillary force to equilibrate gravity. At the top of the contact area between the drop and spindle-knot, which is shown in Fig. 9a, the liquid film begins to break up with an increase in the length of the TCL. Eventually, the volume of the drop becomes large enough that it reaches a critical state and tends to depart from the spindle-knot, and the length of the TCL cannot increase any further. At this moment, the length of the TCL is discussed to evaluate the drop volume at the critical state. Water drops hanging on a fiber usually present two styles, single spindle-knot collection and two spindle-knot collection, as shown in Fig. 9a and b, respectively. These two styles are significant in evaluating the critical volume of a hanging drop because different spindle-knotted fibers have distinct TCL styles. When a water drop tends to depart from one single knot, the TCL is composed of one half-ellipse and two lines, as shown in Fig. 9a. The length of TCL can be estimated as:⁹⁴

$$L \approx \{1/2[2\pi b + 4(a - b)] + 2b\} + 2(m - a) = 2m + \pi b$$

where, 2a and 2b denote as the length and height of the spindle-knot, respectively, and *m* is the contact length between the fiber and the drop. When a water drop tends to depart between two spindle-knots, the TCL is composed of two half-ellipses and two lines, as shown in Fig. 9b. Then the length of the TCL can be estimated as:⁹⁴

$$\begin{split} L &\approx \{1/2[2\pi b_1 + 4(a_1 - b_1)] + 2b_1\} \\ &+ \{1/2[2\pi b_2 + 4(a_2 - b_2)] + 2b_2\} \\ &+ 2(m - a_1 - a_2) = 2m + \pi(b_1 + b_2) \end{split}$$

where, $2a_1$ and $2a_2$ and $2b_1$ and $2b_2$ denote the length and height of the two spindle-knots, respectively. In the case of multi-scale spindle-knots with small spindle-knots as a bridge to settle the water drop, the length of the TCL increases evidently, as shown in Fig. 9c. Similarly, the length of the TCL can be written as:⁶⁴

$$L \approx 2m + \pi(b_1 + b_2) + 2(\pi - 2)(b_3 + b_4 + b_5 + b_6 + b_7)$$

where, $2b_3$, $2b_4$, $2b_5$, $2b_6$ and $2b_7$ are the height of the small spindle-knots. Ideally, if the water drop is collected on two or more identical neighboring spindle-knots, as shown in Fig. 9d, the length of the TCL can be expressed as:⁸³

$$L = 2(n-1)m + 2b(n\pi - \pi - 2n + 4)$$

where, *n* is the number of multiple identical spindle-knots ($n \ge 2$).



Fig. 9 (a) Illustration of water collection on one spindle knot of a bioinspired fiber. (b) Illustration of water collection on two spindle knots of a bioinspired fiber.⁹⁴ (Copyright 2012, American Chemical Society). (c) Illustration of solid–liquid lines when a water drop detaches from the surface of two large spindle knots.⁶⁴ (Copyright 2012, Royal Society of Chemistry). (d) Schematic diagram of the TCL for a water droplet detaching from N spindle knots of a cavity-microfiber.⁸³ (Copyright 2017 Nature). (e) Force analysis of the water drop on two adjacent fibers.⁹⁶ (Copyright 2016, Wiley-VCH).

4.7 Hanging ability

When the drop increases to a critical volume, its hanging ability can be interpreted as a balance between capillary force and the gravity of the drop. A criterion was derived to gauge the drop volume by examining the interplay of surface force and gravity. The component force of surface force in the vertical direction can be expressed as:⁹⁴

$$F_{\rm C} = \gamma L \cos \theta \sin \theta$$

where, γ is the surface tension of water, *L* is the length of the TCL, θ is the apparent contact angle on the fiber surface and α is the off-axis angle. The gravity of the drop can be easily understood as $F_{\rm G} = \rho g v$, where ρ and v are the density and volume of the drop, respectively, and *g* is the gravity acceleration. Equating the component force of surface force and the gravity, $F_{\rm C} = F_{\rm G}$, the volume of the drop is related to the apparent contact angle, the length of TCL and the off-axis angle as follows:^{94,95}

$$V = \frac{\gamma \cos \theta}{\rho g} L \sin \alpha$$

When the drop exactly departs from the fiber, $\sin \alpha$ is very close to 1. If we do not consider the effect of $\sin \alpha$, the maximal volume of drop can be simplified as:^{94,95}

$$V_{\rm m} = \frac{\gamma \, \cos \, \theta}{\rho g} L$$

For different hanging models, the lengths of the TCL can be described as above. If we take the length of the TCL in the function, we can get the specific maximal volume.

4.8 Intersectional configuration

Natural water-collection phenomena depend on the contribution from both the water-collection behaviors of a single fiber and the interplay between fibers. As shown in Fig. 9e, for a drop on two fibers, the resultant force on the vertical direction of the fibers is 0. The only driving force arises from the liquid–gas interfacial tension on the two opposite of the drop. The difference on the two ends makes the drop move towards the crossing site. The driving force can be described as:^{96–98}

$$F = 2\sigma_{l-g}l[\cos(\theta - \alpha) - \cos(\theta + \alpha)]$$

where, σ_{l-g} is the liquid–gas interfacial tension of the drop, l is the length of the contact line between the drop and the fiber, θ is the apparent contact angle on the fiber and α is the half angle between two adjacent fibers. The constant difference of interfacial tension drives the drop to move along the fibers until it is deposited in the crossing site. Considering that the shape of the water drop is almost ellipsoid with one long radius and two equal short radii, the final location of the drop where the driving force equals to 0 can be described as:⁹⁸

$$r = \left(\frac{3V}{4\pi}\right)^{\frac{1}{3}} \frac{1}{\alpha}$$

where r is the distance between the water drop and the intersection of two fibers and V is the volume of the water drop. It is worth noting that the driving force leads to the drop moving away from the knots when the coalesced drop moves to the intersection.

5. Water collection ability

In nature, spider silk has the ability to collect water owing to its distinctive structure. The structure of its spindle-knot overcomes the water hysteresis resistance and achieves directional water transport and coalescence.^{99,100} Consequently, water droplets can condense on its fiber, and the macroscopic water-collection effect can be observed by the integration of these fibers. Recently, researchers have developed several methods to fabricate spindle-knot fibers inspired natural silks and investigated their performances. Here, we discuss the factors affecting the water collection in bioinspired spider silks and their water collection abilities in detail for a better view of the development of water collection materials. In further studies, the growth of water droplets on a single fiber was discussed.^{58,101} As shown in Fig. 10a, the chosen knot was ~41.9 μ m in height and ~128.2 μ m in width. At a low fog flow (~25 cm s⁻¹), the spindle knot collected ~0.83 nL water within \sim 7.2 s, which was almost 15 times its volume and the water collection rate was ~6.92 nL min⁻¹ per knot. At the middle $(\sim 75 \text{ cm s}^{-1})$ and high $(\sim 100 \text{ cm s}^{-1})$ fog flows, the spindleknot collected ~0.8 nL water within only 3 s and 2 s, which are equivalent to ~16 nL min⁻¹ and ~24 nL min⁻¹ per knot, respectively. To clarify the water-collection ability of the spindle-knot, four fibers with different sizes were investigated. When the average volumes of the spindle-knots were 0 nL, 0.03 nL, 0.08 nL and 0.12 nL, the collection velocity increased with the size at a fog flow of \sim 75 cm s⁻¹. As shown in Fig. 10b, the fiber with 0.12 nL spindle-knots collected almost 35 nL water at 12 s and the water collection rate reached 43.75 nL



Fig. 10 (a) Water collection ability of a typical spindle-knot (~41.9 μ m in height and ~128.2 μ m in width) under low (~25 cm s⁻¹), middle (~75 cm s⁻¹), and high (~100 cm s⁻¹) fog flow velocities. (b) Water collection ability of bioinspired artificial spider silks is compared under a fog flow with a velocity of ~75 cm s^{-1.58} (Copyright 2011, Wiley-VCH). (c) Amount of water collected by the membrane increased *versus* spray time. (d) Comparison of collection efficiency between PLLA membrane and PVA membrane.⁹⁸ (Copyright 2016, Wiley-VCH).

min⁻¹ per knot. This indicates that microfibers with larger spindle-knots are significant in water-collection.

Besides the diversity induced by size factor, water-collection ability is also corelated with wettability, structure, topography and external factors. The wettability of spindle-knots and joints can be designed by applying different polymer materials, while smooth and rough structures can be tuned in the solvent atmosphere.⁶¹ In recent research, a smooth hydrophilic surface presented a high water-nucleation density and high coalescence rate compared with a smooth hydrophobic surface.¹⁰² However, there is another situation, the discrepancy in wettability arising from roughness. In a superhydrophobic fiber, the surface presents a higher water-nucleation density and higher shedding rate than the hydrophilic surface. Besides, the water drops tend to pin on the hydrophilic surface.¹⁰³ In the first case, the high coalescence rate originates from the clamshell shape of the drops, giving rise to a large area coverage.¹⁰⁴ In the second case, the higher nucleation density on the superhydrophobic fiber may arise from its large nucleation area. Natural silk exhibits hydrophilic spindle-knots and less hydrophilic joints, which create a surface energy gradient and difference in Laplace pressure. Both high nucleation density and high coalescence rate have important roles in water-collection. Thus, the surface wettability and structure are significant for water-collection efficiency.

For a single fiber, it is beneficial to study and discuss its structure and properties. Extending single fibers to two-dimension membranes will induce macro-characteristics and interplay among fibers. In a recent study, a multi-scale structured membrane composed of hydrophobic poly-L-lactic acid (PLLA) fibers with a radiate distribution was reported.⁹⁸ The morphology of the micrometer-sized bead exhibited nanoscale roughness, which magnified the difference in Laplace pressure. Besides, the macroscopic effect could be magnified by arranging the fiber to form an orderly distribution. Thus, the membrane could achieve highly efficient water-collection ability by integrating millimeter-, micrometer- and nanometerscale structures. In order to evaluate the macroscopic watercapture capacity of the fibrous membrane, it was deposited under an ultrasonic humidifier at 60 cm⁻¹ s⁻¹ fog velocity. Introducing the intersectional configuration, micro-water drops were deposited on the beaded fibers and then transported to the center of the membrane. The relationship between the capacity of collected water and the spray time is shown in Fig. 10c. The maximum value of captured water was 0.39 g and the average water collection rate was 195 μ L min⁻¹. Compared with the hydrophilic PVA membrane, the hydrophobic PLLA membrane exhibits a high water collection efficiency, as showed in Fig. 10d. This phenomenon originates from the low adhesion effect of drops, causing a high watershedding rate. The intersectional configuration makes the surface hydrophobicity dominate in the water-collection process. Thus, the evaluation of microscopic and macroscopic water-collection abilities is beneficial for constructing advanced water-collection materials and devices.

6. Conclusions

Herein, we reviewed the natural spider silk and the recent progress on bioinspired fibers for water-collection application. The silk from the Uloborus walckenaerius spider exhibits excellent water collection performances due to its wet-rebuilding features. The regenerated structure composed of spindle-knots and joints induces the spontaneous transport of droplets, which arises from the surface energy gradient and difference in Laplace pressure. Based on this characteristic, bioinspired fibers have been fabricated via the electrodynamic method, dip-coating method, microfluidic method and fluid-coating method. The electrodynamic method has been developed into a major technique to combine wet-assembly and coaxial electrospinning, which can integrate diverse materials for the construction of hetero-structured fibers. The dip-coating method is a facile strategy to generate spindle-knot fibers due to the Rayleigh instability principle, but this method has the disadvantage of discontinuity. Multilayer and digitally tunable structures can be designed by the microfluidic method and both the microfluidic and fluid-coating methods can fabricate large-scale and continuous fibers, enable exertion in practical application.

Besides, we focused on the water-collection mechanisms and evaluation of water-collection ability. The directional transport of droplets on spindle-knots arises from the coexisting effect of surface energy gradient, difference in Laplace pressure and hysteresis resistance. In addition, the "slope" effect and "curvature" effect generate a high energy barrier to effectively prevent the TCL from receding, while the estimation of the TCL length is a strategy to calculate the maximum volume of hanging drops. Macroscopically, the intersectional configuration facilitates the transport of droplets towards the crossing sites among fibers. However, the abilities of condensation, coalescence and shedding are corelated with size, wettexternal ability, structure, topography and factors. Furthermore, evaluation of water-collection ability on the microscopic and macroscopic scales facilitates the design of water-collection materials and devices with high performance. The exploration of the mechanisms of water collection and the fabrication of bioinspired fibers will help researchers to make progress in water collection, tissue engineering, oil-water separation and biosensors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 51675513 and 51735013).

References

- 1 M. M. Mekonnen and A. Y. Hoekstra, *Sci. Adv.*, 2016, 2, e1500323.
- 2 C. J. Vörösmarty, P. Green, J. Salisbury and R. B. Lammers, *Science*, 2000, **289**, 284–288.
- 3 L. S. Pereira, T. Oweis and A. Zairi, *Agric. Water Manage.*, 2002, **57**, 175–206.
- 4 O. Klemm, R. S. Schemenauer, A. Lummerich,
 P. Cereceda, V. Marzol, D. Corell, J. Van Heerden,
 D. Reinhard, T. Gherezghiher and J. Olivier, *Ambio*, 2012,
 41, 221–234.
- 5 A. F. Batisha, Sustain. Water Qual. Ecol., 2015, 6, 1–10.
- 6 M. Fessehaye, S. A. Abdul-Wahab, M. J. Savage, T. Kohler,
 T. Gherezghiher and H. Hurni, *Renewable Sustainable Energy Rev.*, 2014, 29, 52–62.
- 7 J. de Dios Rivera and D. Lopez-Garcia, *Atmos. Res.*, 2015, **151**, 250–258.
- 8 B. White, A. Sarkar and A. M. Kietzig, *Appl. Surf. Sci.*, 2013, **284**, 826–836.
- 9 S. Montecinos, D. Carvajal, P. Cereceda and M. Concha, *Atmos. Res.*, 2018, **209**, 163–169.
- 10 C. J. Ma, M. Kasahara and S. Tohno, *Atmos. Environ.*, 2003, 37, 3749–3756.
- 11 J. de Dios Rivera, Atmos. Res., 2011, 102, 335-342.
- 12 Y. Zheng, H. Bai, Z. Huang, X. Tian, F. Nie, Y. Zhao, J. Zhai and L. Jiang, *Nature*, 2010, **463**, 640.
- 13 J. Ju, H. Bai, Y. Zheng, T. Zhao, R. Fang and L. Jiang, *Nat. Commun.*, 2012, 3, 1247.
- 14 A. R. Parker and C. R. Lawrence, Nature, 2001, 414, 33.
- 15 V. Sharma, M. Sharma, S. Kumar and V. Krishnan, *Flora*, 2016, 224, 59–65.
- 16 Z. Pan, W. G. Pitt, Y. Zhang, N. Wu, Y. Tao and T. T. Truscott, *Nat. Plants*, 2016, 2, 16076.
- 17 H. Andrews, E. Eccles, W. Schofield and J. Badyal, *Langmuir*, 2011, 27, 3798–3802.
- 18 M. Gürsoy, M. Harris, J. Downing, S. Barrientos-Palomo, A. Carletto, A. Yaprak, M. Karaman and J. Badyal, *Colloids Surf.*, A, 2017, 529, 195–202.
- 19 M. Gürsoy, M. Harris, A. Carletto, A. Yaprak, M. Karaman and J. Badyal, *Colloids Surf.*, A, 2017, **529**, 959–965.
- 20 H. Zhu, Z. Guo and W. Liu, Chem. Commun., 2016, 52, 3863-3879.
- 21 L. Zhong, H. Zhu, Y. Wu and Z. Guo, J. Colloid Interface Sci., 2018, **525**, 234–242.
- 22 H. Zhu and Z. Guo, Chem. Commun., 2016, 52, 6809-6812.
- 23 H. Zhu, F. Yang, J. Li and Z. Guo, *Chem. Commun.*, 2016, 52, 12415–12417.
- 24 L. Zhong, R. Zhang, J. Li, Z. Guo and H. Zeng, *Langmuir*, 2018, 34, 15259–15267.
- 25 L. Zhong, J. Feng and Z. Guo, *J. Mater. Chem. A*, 2019, 7, 8405–8413.
- 26 Y. Jun, E. Kang, S. Chae and S. H. Lee, *Lab Chip*, 2014, **14**, 2145–2160.
- 27 J. Zhang, X. Pan, Q. Xue, D. He, L. Zhu and Q. Guo, J. Membr. Sci., 2017, 532, 38–46.

- 28 M. A. Daniele, D. A. Boyd, D. R. Mott and F. S. Ligler, *Biosens. Bioelectron.*, 2015, 67, 25–34.
- 29 F. G. Omenetto and D. L. Kaplan, *Science*, 2010, **329**, 528–531.
- 30 Z. Zhou, S. Zhang, Y. Cao, B. Marelli, X. Xia and T. H. Tao, *Adv. Mater.*, 2018, **30**, 1706983.
- 31 H. Elettro, S. Neukirch, F. Vollrath and A. Antkowiak, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 6143–6147.
- 32 J. A. Kluge, O. Rabotyagova, G. G. Leisk and D. L. Kaplan, *Trends Biotechnol.*, 2008, **26**, 244–251.
- 33 J. Gosline, P. Guerette, C. Ortlepp and K. Savage, J. Exp. Biol., 1999, 202, 3295–3303.
- 34 H. Peters, Zoomorphology, 1984, 104, 96-104.
- 35 D. Porter and F. Vollrath, *Adv. Mater.*, 2009, **21**, 487–492.
- 36 H. Bai, J. Ju, Y. Zheng and L. Jiang, Adv. Mater., 2012, 24, 2786–2791.
- 37 Y. Chen and Y. Zheng, Nanoscale, 2014, 6, 7703-7714.
- 38 F. Vollrath and D. T. Edmonds, *Nature*, 1989, **340**, 305.
- 39 A. Rising and J. Johansson, Nat. Chem. Biol., 2015, 11, 309.
- 40 O. Emile, A. Le Floch and F. Vollrath, *Nature*, 2006, **440**, 621.
- 41 A. Greiner and J. H. Wendorff, *Angew. Chem., Int. Ed.*, 2007, 46, 5670–5703.
- 42 D. Li and Y. Xia, Adv. Mater., 2004, 16, 1151-1170.
- 43 R. Jaeger, H. Schönherr and G. J. Vancso, *Macromolecules*, 1996, **29**, 7634–7636.
- 44 H. Fong, I. Chun and D. Reneker, *Polymer*, 1999, **40**, 4585–4592.
- 45 Y. Zhang, Y. Tian, L. Xu, C. Wang and S. Chen, *Chem. Commun.*, 2015, **51**, 17525–17528.
- 46 Y. Jin, D. Yang, D. Kang and X. Jiang, *Langmuir*, 2009, 26, 1186–1190.
- 47 W. Yuan and K. Zhang, Langmuir, 2012, 28, 15418–15424.
- 48 Y. Zhan and S. Yu, J. Am. Chem. Soc., 2008, 130, 5650–5651.
- 49 C. Song, L. Zhao, W. Zhou, M. Zhang and Y. Zheng, J. Mater. Chem. A, 2014, 2, 9465–9468.
- 50 L. Zhao, C. Song, M. Zhang and Y. Zheng, Chem. Commun., 2014, 50, 10651–10654.
- 51 X. Tian, H. Bai, Y. Zheng and L. Jiang, *Adv. Funct. Mater.*, 2011, **21**, 1398–1402.
- 52 H. Dong, N. Wang, L. Wang, H. Bai, J. Wu, Y. Zheng,
 Y. Zhao and L. Jiang, *ChemPhysChem*, 2012, 13, 1153–1156.
- 53 N. Thakur, A. S. Ranganath, K. Agarwal and A. Baji, *Macromol. Mater. Eng.*, 2017, **302**, 1700124.
- 54 J. E. Díaz, A. Barrero, M. Márquez and I. G. Loscertales, *Adv. Funct. Mater.*, 2006, **16**, 2110–2116.
- 55 J. H. Park and P. V. Braun, Adv. Mater., 2010, 22, 496–499.
- 56 A. Nandakumar, R. Truckenmüller, M. Ahmed,
 F. Damanik, D. R. Santos, N. Auffermann, J. de Boer,
 P. Habibovic, C. van Blitterswijk and L. Moroni, *Small*, 2013, 9, 3405–3409.
- 57 X. Tian, Y. Chen, Y. Zheng, H. Bai and L. Jiang, Adv. Mater., 2011, 23, 5486–5491.
- 58 H. Bai, J. Ju, R. Sun, Y. Chen, Y. Zheng and L. Jiang, Adv. Mater., 2011, 23, 3708–3711.

- 59 D. Quéré, J. M. Di Meglio and F. Brochard-Wyart, *Science*, 1990, 249, 1256–1260.
- 60 D. Quéré, Annu. Rev. Fluid Mech., 1999, 31, 347-384.
- 61 H. Bai, X. Tian, Y. Zheng, J. Ju, Y. Zhao and L. Jiang, *Adv. Mater.*, 2010, 22, 5521–5525.
- 62 S. Feng, Y. Hou, Y. Chen, Y. Xue, Y. Zheng and L. Jiang, J. Mater. Chem. A, 2013, 1, 8363–8366.
- 63 Y. Chen, L. Wang, Y. Xue, Y. Zheng and L. Jiang, Soft Matter, 2012, 8, 11450–11454.
- 64 Y. Hou, Y. Chen, Y. Xue, L. Wang, Y. Zheng and L. Jiang, Soft Matter, 2012, 8, 11236–11239.
- 65 Y. Song, Y. Liu, H. Jiang, S. Li, C. Kaya, T. Stegmaier, Z. Han and L. Ren, *Sci. Rep.*, 2017, 7, 12056.
- 66 Y. Chen, L. Wang, Y. Xue, L. Jiang and Y. Zheng, *Sci. Rep.*, 2013, 3, 2927.
- 67 S. Wang, S. Feng, Y. Hou and Y. Zheng, *Macromol. Rapid Commun.*, 2015, 36, 459–464.
- 68 Y. Chen, J. He, L. Wang, Y. Xue, Y. Zheng and L. Jiang, J. Mater. Chem. A, 2014, 2, 1230–1234.
- 69 W. Jeong, J. Kim, S. Kim, S. Lee, G. Mensing and D. J. Beebe, *Lab Chip*, 2004, 4, 576–580.
- 70 S. J. Shin, J. Y. Park, J. Y. Lee, H. Park, Y. D. Park, K. B. Lee, C. M. Whang and S. H. Lee, *Langmuir*, 2007, 23, 9104–9108.
- 71 E. Kang, G. S. Jeong, Y. Y. Choi, K. H. Lee, A. Khademhosseini and S. H. Lee, *Nat. Mater.*, 2011, 10, 877.
- 72 Z. Wu, J. Wang, Z. Zhao, Y. Yu, L. Shang and Y. Zhao, *ChemPhysChem*, 2018, **19**, 1990–1994.
- 73 J. Wang, M. Zou, L. Sun, Y. Cheng, L. Shang, F. Fu and Y. Zhao, *Sci. China Mater.*, 2017, **60**, 857–865.
- 74 Y. Cheng, F. Zheng, J. Lu, L. Shang, Z. Xie, Y. Zhao,
 Y. Chen and Z. Gu, *Adv. Mater.*, 2014, 26, 5184–5190.
- 75 Y. Cheng, Y. Yu, F. Fu, J. Wang, L. Shang, Z. Gu and Y. Zhao, ACS Appl. Mater. Interfaces, 2016, 8, 1080–1086.
- 76 L. Shang, F. Fu, Y. Cheng, Y. Yu, J. Wang, Z. Gu and Y. Zhao, Small, 2017, 13, 1600286.
- 77 L. Shang, Y. Wang, Y. Yu, J. Wang, Z. Zhao, H. Xu and Y. Zhao, *J. Mater. Chem. A*, 2017, 5, 15026–15030.
- 78 X. He, W. Wang, Y. Liu, M. Jiang, F. Wu, K. Deng, Z. Liu, X. Ju, R. Xie and L. Chu, ACS Appl. Mater. Interfaces, 2015, 7, 17471–17481.
- 79 P. Zhu, T. Kong, Z. Kang, X. Tian and L. Wang, Sci. Rep., 2015, 5, 11102.
- 80 G. Vladisavljević, R. Al Nuumani and S. Nabavi, *Micromachines*, 2017, 8, 75.
- 81 C. Liu, W. Zheng, R. Xie, Y. Liu, Z. Liang, G. Luo, M. Ding and Q. Liang, *Chin. Chem. Lett.*, 2019, **30**, 457–460.
- 82 X. Ji, S. Guo, C. Zeng, C. Wang and L. Zhang, *RSC Adv.*, 2015, 5, 2517–2522.
- 83 Y. Tian, P. Zhu, X. Tang, C. Zhou, J. Wang, T. Kong, M. Xu and L. Wang, *Nat. Commun.*, 2017, 8, 1080.
- 84 Y. Tian, J. Wang and L. Wang, ACS Appl. Mater. Interfaces, 2018, 10, 29219–29226.
- 85 Q. Peng, H. Shao, X. Hu and Y. Zhang, *Macromol. Mater.* Eng., 2017, 302, 1700102.

- 86 H. Bai, R. Sun, J. Ju, X. Yao, Y. Zheng and L. Jiang, *Small*, 2011, 7, 3429–3433.
- 87 A. De Ryck and D. Quéré, Langmuir, 1998, 14, 1911-1914.
- 88 Y. Xue, Y. Chen, T. Wang, L. Jiang and Y. Zheng, J. Mater. Chem. A, 2014, 2, 7156–7160.
- 89 É. Lorenceau and D. Quéré, J. Fluid Mech., 2004, 510, 29– 45.
- 90 M. K. Chaudhury and G. M. Whitesides, Science, 1992, 256, 1539–1541.
- 91 D. Quéré, M. J. Azzopardi and L. Delattre, *Langmuir*, 1998, 14, 2213–2216.
- 92 D. Quéré, A. Lafuma and J. Bico, *Nanotechnology*, 2003, 14, 1109.
- 93 S. Feng, Y. Hou, Y. Xue, L. Gao, L. Jiang and Y. Zheng, Soft Matter, 2013, 9, 9294–9297.
- 94 Y. Hou, Y. Chen, Y. Xue, Y. Zheng and L. Jiang, *Langmuir*, 2012, 28, 4737–4743.
- 95 É. Lorenceau, C. Clanet and D. Quéré, *J. Colloid Interface Sci.*, 2004, **279**, 192–197.

- 96 H. Dong, Y. Zheng, N. Wang, H. Bai, L. Wang, J. Wu, Y. Zhao and L. Jiang, *Adv. Mater. Interfaces*, 2016, 3, 1500831.
- 97 X. Ma, M. Cao, C. Teng, H. Li, J. Xiao, K. Liu and L. Jiang, J. Mater. Chem. A, 2015, 3, 15540–15545.
- 98 M. Du, Y. Zhao, Y. Tian, K. Li and L. Jiang, Small, 2016, 12, 1000–1005.
- 99 Y. Cui, D. Li and H. Bai, *Ind. Eng. Chem. Res.*, 2017, 56, 4887-4897.
- 100 J. Li and Z. Guo, Nanoscale, 2018, 10, 13814-13831.
- 101 Y. Chen, D. Li, T. Wang and Y. Zheng, *Sci. Rep.*, 2016, 6, 19978.
- 102 X. Dai, N. Sun, S. O. Nielsen, B. B. Stogin, J. Wang, S. Yang and T. S. Wong, *Sci. Adv.*, 2018, 4, eaaq0919.
- 103 Q. Zhang, G. Lin and J. Yin, *Soft Matter*, 2018, 14, 8276–8283.
- 104 R. De Ruiter, J. de Ruiter, H. B. Eral, C. Semprebon, M. Brinkmann and F. Mugele, *Langmuir*, 2012, 28, 13300– 13306.