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Bioinspired One-Dimensional Materials for Directional Liquid Transport

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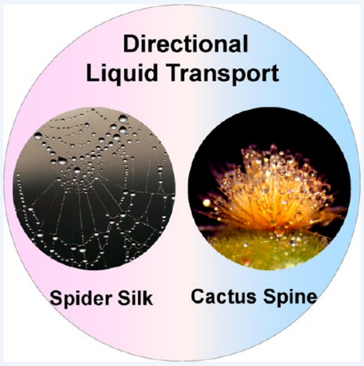

CONSPECTUS: One-dimensional materials (1D) capable of transporting liquid droplets directionally, such as spider silks and cactus spines, have recently been gathering scientists' attention due to their potential applications in microfluidics, textile dyeing, filtration, and smog removal. This remarkable property comes from the arrangement of the micro- and nanostructures on these organisms' surfaces, which have inspired chemists to develop methods to prepare surfaces with similar directional liquid transport ability. In this Account, we report our recent progress in understanding how this directional transport works, as well our advances in the design and fabrication of bioinspired 1D materials capable of transporting liquid droplets directionally.

To begin, we first discuss some basic theories on droplet directional movement. Then, we discuss the mechanism of directional transport of water droplets on natural spider silks. Upon contact with water droplets, the spider silk undergoes what is known as a wet-rebuilt, which forms periodic spindle-knots and joints. We found that the resulting gradient of Laplace pressure and surface free energy between the spindle-knots and joints account for the cooperative driving forces to transport water droplets directionally. Next, we discuss the directional transport of water droplets on desert cactus. The integration of multilevel structures of the cactus and the resulting integration of multiple functions together allow the cactus spine to transport water droplets continuously from tip to base.

Based on our studies of natural spider silks and cactus spines, we have prepared a series of artificial spider silks (A-SSs) and artificial cactus spines (A-CSs) with various methods. By changing the surface roughness and chemical compositions of the artificial spider silks' spindle-knots, or by introducing stimulus-responsive molecules, such as thermal-responsive and photoresponsive molecules, onto the spindle-knots, we can reversibly manipulate the direction of water droplet's movement on the prepared A-SSs. In addition, the A-SSs with nonuniform spindle-knots, such as multilevel sized spindle-knots and gradient spindle-knots, further demonstrate integrated directional transport ability for water droplets. Through mimicking the main principle of cactus spines in transporting water droplets, we were able to fabricate both single and array A-CSs, which are able to transport liquid droplets directionally both in air and under water.

Lastly, we demonstrated some applications of this directional liquid transport, from aspects of efficient fog collection to oil/water separation. In addition, we showed some potential applications in smart catalysis, tracer substance enrichment, smog removal, and drug delivery.

INTRODUCTION

Recently, surfaces capable of transporting liquid droplets have attracted considerable attention due to their close relevance to people's daily life and commercial run. In nature, surfaces capable of transporting liquid droplets are ubiquitous. For instance, butterfly wings,[1,2] rice leaves,[3,4] and feathers of ducks and geese[5] all show preferential directions in shedding off water droplets. The directional arrangement of the micro- and nanostructures on these organism surfaces proves to account for this unique property. Inspired by these special surfaces, various methods have been developed to prepare surfaces with similar directional liquid transport ability.[6,7]

Comparing with the two-dimensional (2D) surfaces, one-dimensional (1D) materials capable of transporting liquid droplets directionally have aroused even more interest because of their potential applications in microfluidics, textile dyeing, filtration, and smog removal. To transport liquid droplet directionally, these 1D materials are usually characterized of gradient in shape[8] or gradient in surface wettability.[9] As a typical example, spider silk takes advantage of the synergetic effect of both shape and wettability gradient between spindle-knots and joints, transporting water droplets directionally from joints to spindle-knots.[10] Besides the spider silk, the well-known drought-tolerant cactus also exploits integration of shape and wettability gradient along a single cactus spine, producing a directional liquid transport system.[11]

In this Account, we will review our recent progress in researching into 1D materials for directional liquid transport, from natural to artificial materials, and also demonstrate some

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related applications. First, we will present some basic theories on a droplet's directional movement, focusing on analysis of driving and resistance forces. Second, we will demonstrate the origin of the beautiful scenery of a morning spider web decorated with blinking water droplets and reveal the mystery of the desert cactus' drought-tolerance. In the third part, the A-SSs with uniform and nonuniform spindle-knots as well as A-CSs in manipulating liquid transport will be introduced. In the fourth part, some applications of directional liquid transport in efficient fog collection and oil/water separation will be shown. Finally, we will give a brief conclusion and outlook.

1. BASIC THEORY ON DROPLET DIRECTIONAL MOVEMENT

Generally, a stationary droplet on a solid surface is subjected to counterbalanced external forces. However, once the external forces cannot be balanced, the droplet will move toward a specific direction, that is, perform directional movement. In general terms, these various movements can be classified into two types: movements induced by the nonuniform surface wettability[12,13] and movements induced by the asymmetrical geometric shape of the substrate.[8]

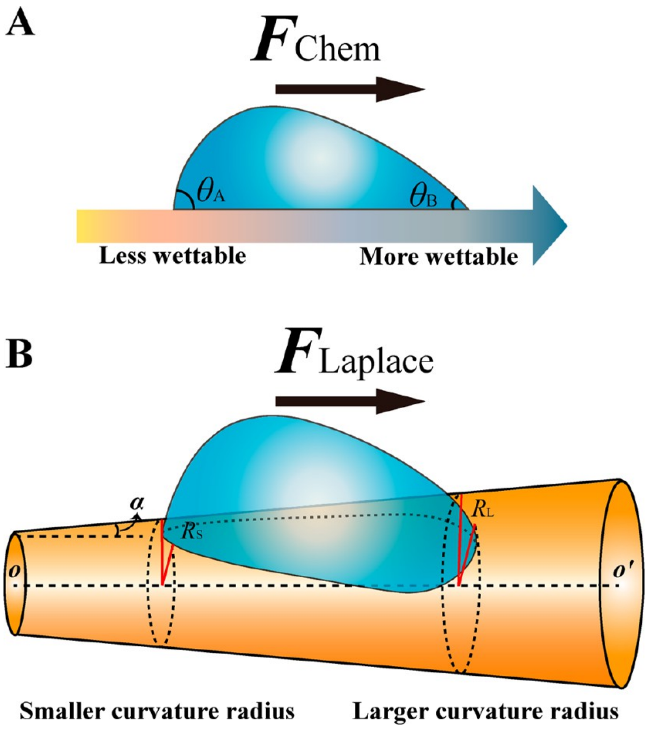

Figure 1. Driving forces for directional movement of liquid droplets. (A) Driving force arising from surface wettability gradient (F_{Chem}) propels liquid droplets toward more wettable region. (B) Driving force arising from shape gradient (F_{Laplace}) propels liquid droplet toward region with larger curvature radius.

Nonuniform surface wettability can be generated by many means, such as premodifying a homogeneous surface unevenly,[14] taking advantage of chemicals contained in moving droplet to covalently bond to[15−17] or physically adsorb[18] on the underlying substrate and causing an asymmetric wettability in front and rear of the droplet, asymmetrically photoirradiating surfaces covered with photoisomerizable monolayer,[19] heating or cooling surface locally,[20] creating surface roughness difference[21] (like the different arrangement of fibril on the spindle-knot and joint of spider silk and width-changing grooves on the cactus spine), and so on. In these cases, the driving force F_{Chem} is proportional to the gradient of the surface wettability (Figure 1A). As liquid contact angle is usually used to assess the wettability of a solid surface, the driving force can thus be described as

$$F_{\mathrm{Chem}} \sim \pi R_0 \gamma (\cos \theta_B - \cos \theta_A) \tag{1}$$

where R_0 is the radius of the droplet, γ is the surface tension, θ_A and θ_B are the contact angles at less wettable and more wettable side of the droplet, respectively.

With regard to droplet movement on the asymmetric-shaped substrate, such as cone fibers,[8] cone tubes,[9] and other space-confined regions,[22] the driving force arises from the gradient of Laplace pressure inside the droplet. Take a water droplet on a cone-structured object as an example (Figure 1B), the driving force F_{Laplace} can be expressed as

$$F_{\mathrm{Laplace}} \sim -\int_{R_S}^{R_L} \frac{2\gamma}{(R + R_0)^2} \sin \alpha \, dz \tag{2}$$

where R is the local radius of the cone-structured object, R_S and R_L are the local radii of the object at the two opposite sides of the droplet, α is the half apex angle of the cone, and dz is the minute incremental radius along the cone. Besides these two main situations, a chemically homogeneous flat surface with stiffness gradient can also drive liquid droplets toward a softer region due to the different deforming degree of the substrate and the resulting change in apparent contact angles.[23] In addition, by means of electric field, an ionic liquid droplet can be pumped along conductive nanowire smoothly from cathode to anode.[24] All of these driving forces can be solely or cooperatively harnessed by 1D material for directional liquid transport.

On most occasions, due to the surface inhomogeneity, motions of droplets with low viscosity are subjected to resistance force F_{Res}. The F_{Res} is caused by the contact angle hysteresis (difference between the advancing contact angle θ_{Adv} and receding contact angle θ_{Rec} of a droplet) and can be calculated as

$$F_{\mathrm{Res}} \sim \pi R_0 \gamma (\cos \theta_{\mathrm{Res}} - \cos \theta_{\mathrm{Adv}}) \tag{3}$$

As a result, smaller hysteresis in contact angles favors a droplet's directional movement.

2. DIRECTIONAL WATER DROPLET TRANSPORT ON NATURAL SPIDER SILKS AND NATURAL CACTUS SPINES

2.1. Directional Water Droplet Transport on Natural Spider Silks

People may have the experience of being fascinated by the beautiful spider web decorated with glittering water droplets in early morning. Further in-depth observation shows that these droplets distribute periodically on the spider silks.[10] Since surface properties of an object depend heavily on its microstructures, this unique patterning of water droplets implies special structures of spider silks. Exactly, as shown in Figure 2A−E, the typical structures of wet-rebuilt spider silk (capture silk of *Cribellate* spider) are characterized of periodic spindle-knots and joints, with spindle-knots being conical (Figure 2A). Magnified images show that the spindle-knots (Figure 2B, C) and joints (Figure 2D, E) are composed of random and aligned nanofibrils, respectively. This difference in

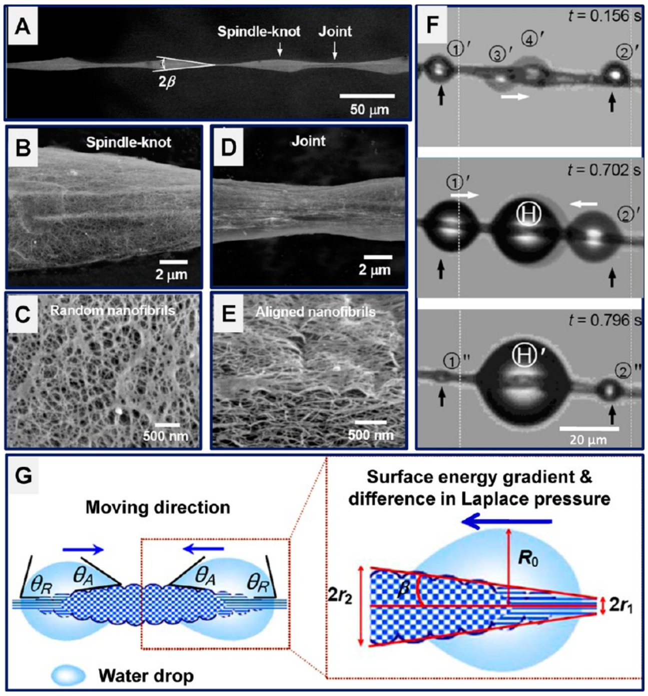

Figure 2. Microstructures of spider silk and directional transport of water droplets on it. (A) The wet-rebuilt spider silk is composed of periodic spindle-knots with random nanofribrils (B, C) and joints with aligned nanofribrils (D, E). (F) Directional transport of water droplets on the spider silk. Tiny water droplets move from joints toward knots. (G) Mechanism of the directional transport of water droplets. The surface free energy gradient and Laplace pressure gradient drive together water droplets to move directionally.

the nanofibrils' arrangement results in a difference in surface roughness and hence a difference in surface wettability, with the rougher spindle-knots being more wettable.

As tiny water droplets in fog deposit on the spider silk (Figure 2F), water droplets on the joints increase their volume and move directionally toward the spindle-knots (denoted as white arrows). In this process, the driving force arising from the difference in Laplace pressure inside the droplet and the driving force arising from the difference in surface free energy between spindle-knot and joint cooperate together, driving water droplet to move directionally (Figure 2G). In addition to the cooperation between these two actuation forces, the wet-rebuilt structures also optimize a hysteresis effect to favor this directional movement. Specifically, the three-phase contact lines (TCLs) of water droplets are discontinuous on the spindle-knots but continuous on the joints. Moreover, the continuous TCLs on the joints are parallel to the axial direction of the spider silk. All of these factors lead to a more noticeable hysteresis effect on the spindle-knots than on the joints; therefore, water droplets on the joints are transported more readily.

2.2. Directional Water Droplet Transport on Natural Cactus Spines

Besides the periodical directional transport of water droplets on natural spider silks, the natural cactus spine is found to be capable of transporting water droplets consistently in a specific direction due to the existing of an integrated transport system.[11] The cacti are well-known for their capability to thrive in extreme water-shortage deserts. Other than the general consideration of minimizing water evaporation loss passively, we find recently that the cactus *Opuntia microdasys* still gets water positively by directionally transporting water droplets deposited on their spines and absorbing the water into its body finally.

Figure 3A shows a typical cluster of the cactus spines and trichomes, which distribute evenly on the stem of the cactus. As can be seen, spines growing in arbitrary directions form a hemispherical shape. Each spine can further be divided into three parts with different features (Figure 3B): the tip with oriented conical barbs (Figure 3C, F), the middle with gradient grooves (Figure 3D, E), and the base with belt-structured trichomes. These structural features facilitate directional transport of water droplets from the very tip toward base of the spine. In particular, the conical shape of the spine results in

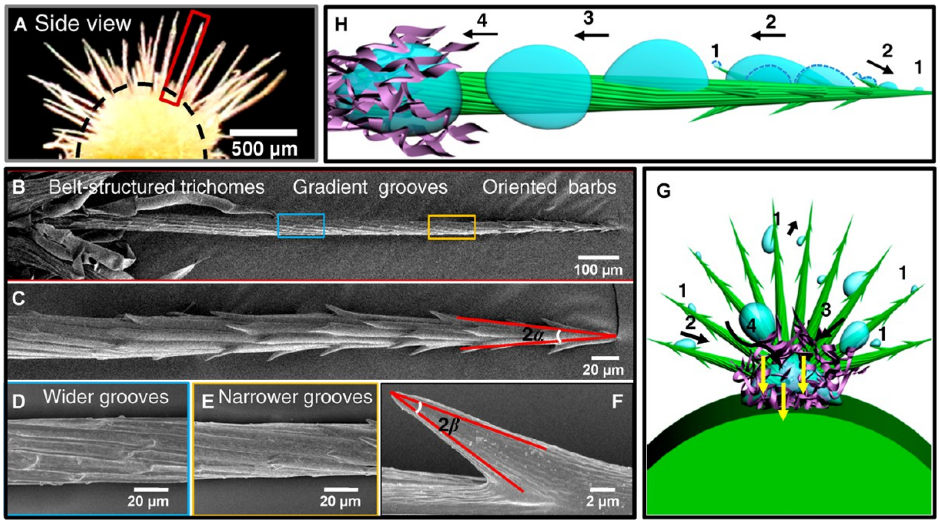

Figure 3. Microstructures of cactus and directional water transport system on it. (A) Single cluster of cactus spines and trichomes with each spine integrated of three parts (B): the tip with oriented conical barbs (C, F), the middle with gradient grooves (D, E), and the base with belt-structured trichomes. (H) Schematic illustration of the entire process of water droplets' directional transport from tip to base of a cactus spine. (G) Model of the directional water transport system on cactus.

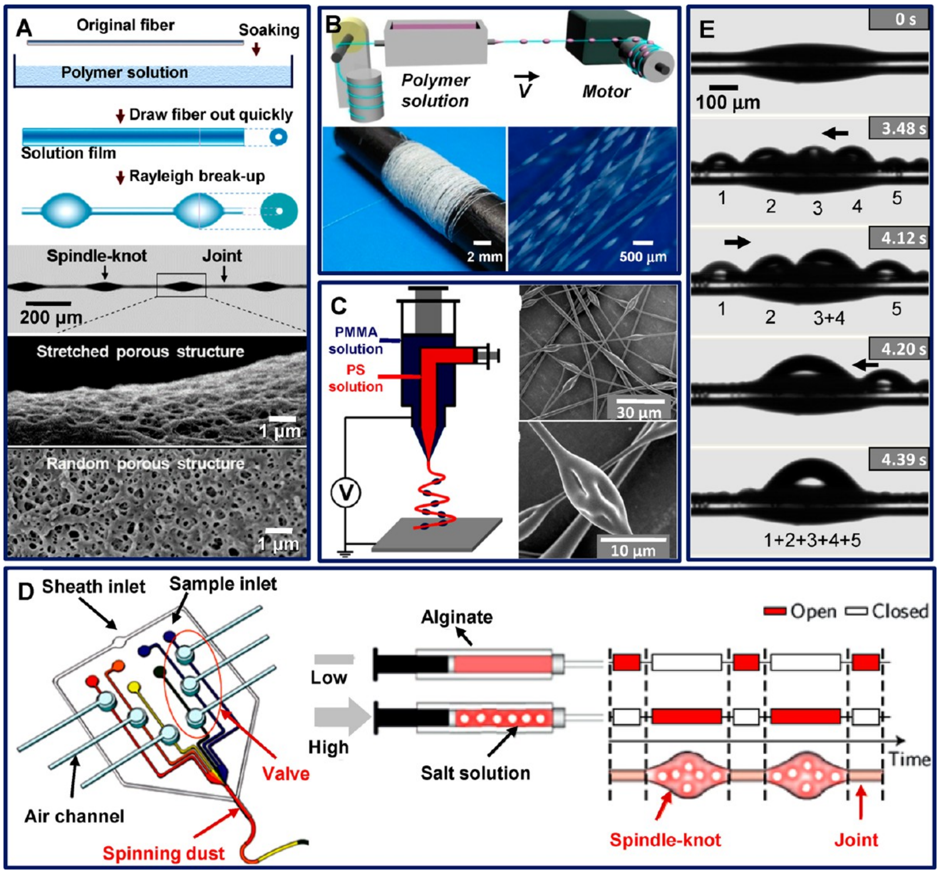

Figure 4. Various methods to prepare A-SSs: By means of (A) dip-coating, (B) fluid-coating, (C) electrodynamics technology, and (D) digital microfluidic systems, A-SSs with morphology (the insets in B) and fine structures (the insets in A and C) similar to that of natural spider silks can be prepared. (E) A-SSs can transport water droplets directionally.

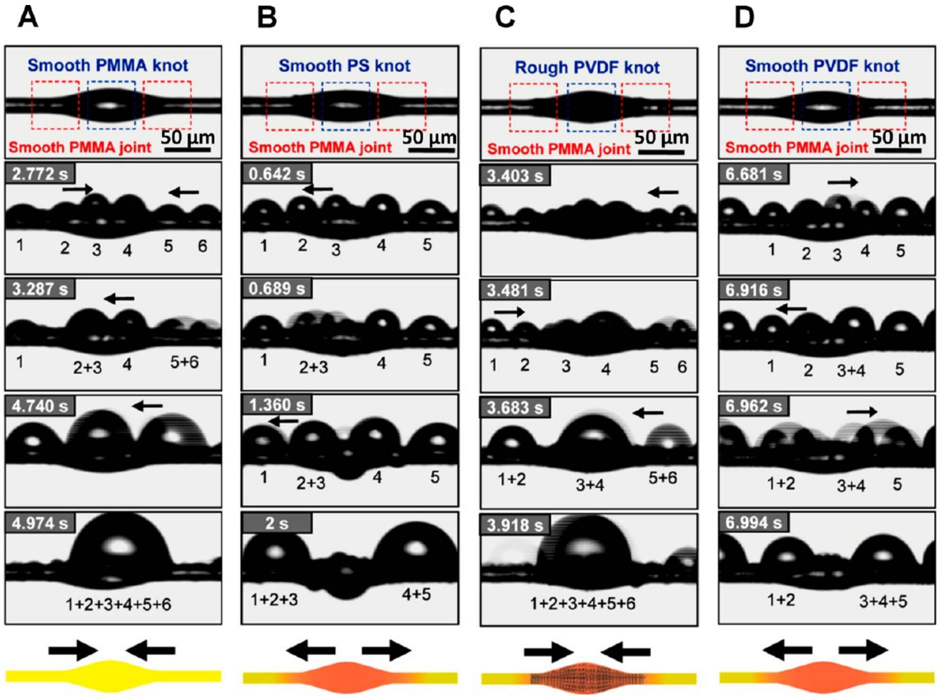

Figure 5. Direction controlled transport of water droplets on A-SSs. Through changing the spindle-knots' chemical composition (A, B) and surface roughness (C, D), the A-SSs can transport water droplet toward and away from the spindle-knots.

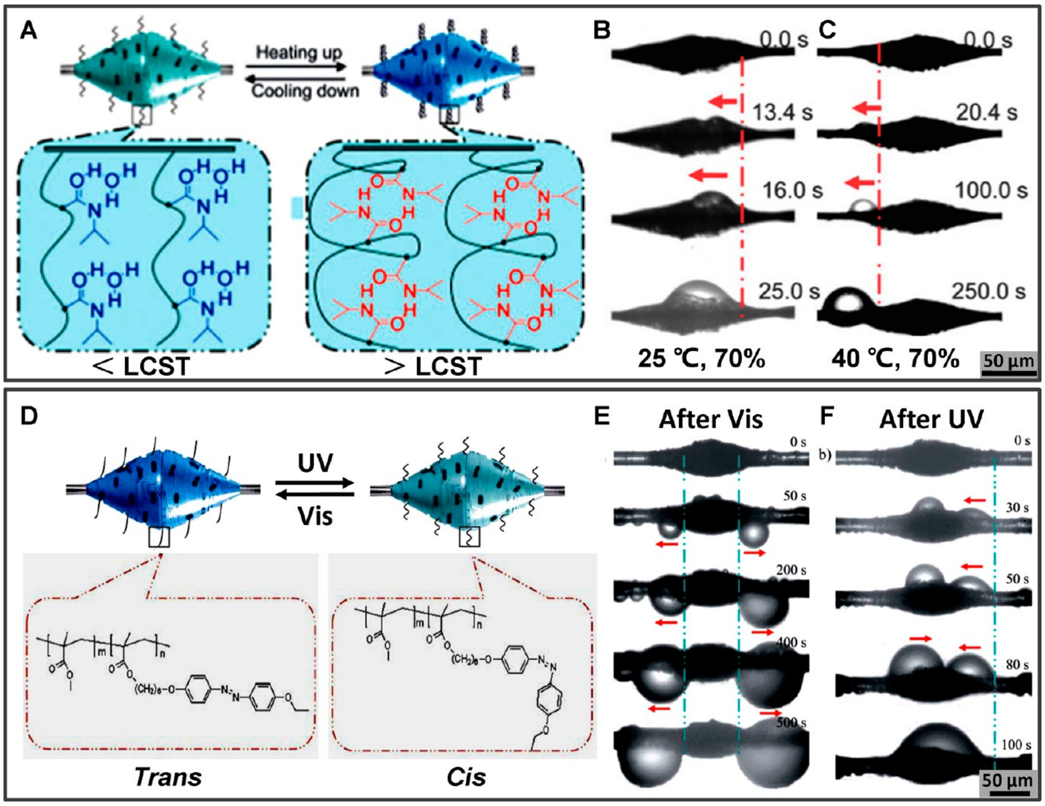

Figure 6. Stimulus-responsive transport of water droplets on A-SSs. Modifying spindle-knots with thermal-responsive PNIPAAm containing polymer (A) and photoresponsive azobenzene-contained polymer (D), the A-SSs can transport water droplet toward (B, F) or away from (C, E) the spindle-knots in situ under appropriate stimuli.

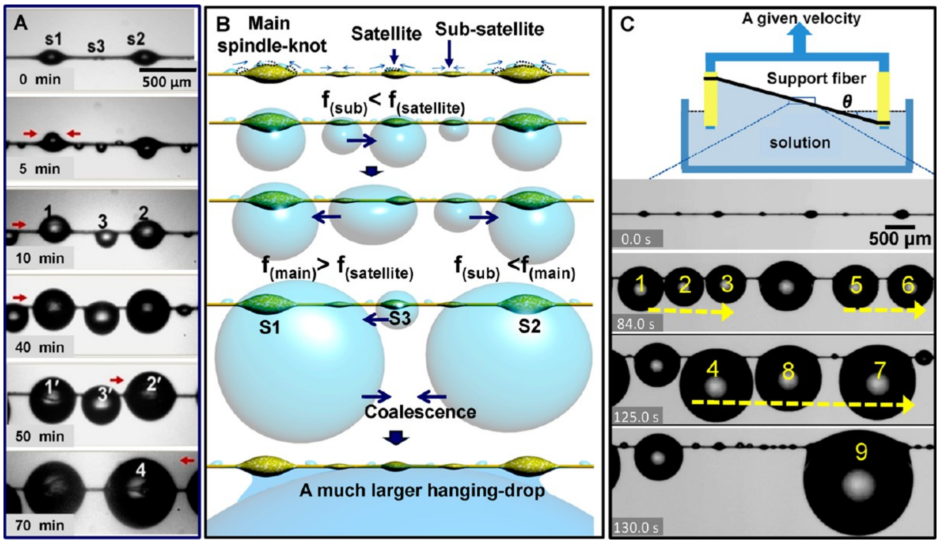

Figure 7. Integrated transport of water droplets on A-SSs with nonuniform spindle-knots. Optical observation (A) and schematic illustration (B) of directional transport of water droplets on the A-SSs with multileveled spindle-knots. (C) Setup for fabricating A-SSs with gradient spindle-knots and the directional transport of water droplets on the as prepared A-SS (D).

a gradient of Laplace pressure inside the water droplet, which drives it to move toward region with larger curvature radius. The oriented barbs in the tip also supply anisotropic contact angle hysteresis, making it easier for the droplet to move toward the base side. After the droplet moves into the middle region, the gradient grooves produce a roughness gradient and thus a wettability gradient, driving the water droplet still moving toward the base side. As the water droplet moves closer to the base, it is absorbed immediately by the hydrophilic trichomes due to the strong capillary force. In this manner, the water droplet finishes a complete process of directional movement from the tip to the base of the spine (see Figure 3H). Notably, by integrating the interaction between multiple spines, spines and trichomes, and trichomes and trichomes, the cactus developed a water directional transport system, realizing continuous and efficient collection and transportation of water droplets (Figure 3G).

3. DIRECTIONAL WATER DROPLET TRANSPORT ON A-SSs AND A-CSs

3.1. Directional Water Droplet Transport on A-SSs with Uniform Spindle-Knots

Inspired by the relationship between spider silk's unique structural features and its ability to transport water droplets directionally, various methods have been developed to fabricate fibers with structures resembling natural spider silks, which we call here A-SSs. These A-SSs demonstrate similar capability of transporting water droplets directionally.

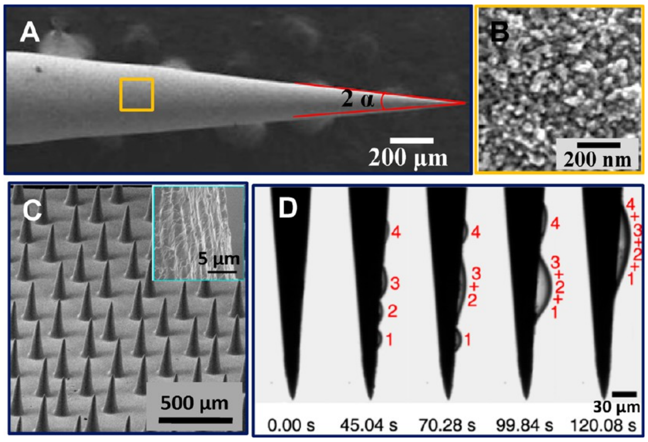

Figure 8. SEM images of a single A-CS (A) with homogeneous nanostructures (B). (C) Array of the A-CSs with the inset showing the ridged structures on each spine. (D) Directional oil droplet transport on a single A-CS under water.

A-SSs Capable of Transporting Water Droplets toward Spindle-Knots. First, an ordinary dip-coating method[10] was exploited to prepare the A-SSs. As shown in Figure 4A, through immersing a uniform fiber into a polymer solution and drawing it out horizontally, a thin layer of polymer solution is formed on the fiber followed by breaking into a series of solution droplets distributing periodically on the fiber due to Rayleigh instability. After these droplets dried, the A-SSs with periodic spindle-knots and joints can be got. The inset scanning electron microscoy (SEM) characterizations of the as prepared A-SSs give similar fine structures to that of the natural spider silk. Following the same dip-coating concept and combining the breath figure technology, a series of A-SSs with tunable microporous-structured (smooth, less porous, homogeneous porous, gradient porous, and dented) spindle-knots can be prepared.[25] Besides the dip-coating method, a fluid-coating method suitable for large scale fabrication of A-SSs was developed (Figure 4B).[26] A nylon fiber is horizontally fixed to pass through a polymer reservoir. A motor connected to the end of the fiber was used to drag the fiber at a specific speed. After the fiber is steadily drawn out of the polymer reservoir, it is coated with a layer of polymer solution. The following processes of polymer solution film breaking up and formation of the periodic spindle-knots are the same as that in dip-coating method. Figure 4C gives an electrohydrodynamics method to prepare the A-SSs.[27,28] A coaxial electrospinning device is used with dilute poly(methyl methacrylate) (PMMA) solution and concentrated polystyrene (PS) solution working as the outer and inner solutions, respectively. When a high-voltage electric field is applied, the viscous PS solution stretches into liquid thread whereas the PMMA solution flows out and adheres on the PS thread. The PMMA solution film then breaks into discontinuous liquid droplets and solidifies into periodic spindle-knots on the PS fiber. Beyond those, mimicking the silk-spinning process, researchers used a microfluidic system consisting of digital and programmable flow controller, realizing continuous fabrication of A-SSs (Figure 4D).[29] By modulating the valve operation of two channels with different fluids, the morphology and fine structures of the resulting fibers can be strictly controlled. Through introducing an alginate solution containing salt at a high feeding rate into one of the channel and afterward removing the salt by dissolution, porous spindle-knotted fibers can be obtained. All of the A-SSs prepared using the aforementioned methods have uniform spindle-knots, they are capable of transporting water droplets directionally from joints toward spindle-knots; see Figure 4E.

A-SSs Capable of Transporting Water Droplets Reversibly. Generally, water droplets move directionally from joints to spindle-knots both on natural and ordinary A-SSs. In fact, the inversive movement of water droplet on A-SSs, that is, movement from spindle-knots to joints, can also be accomplished by changing the knots' wettability through altering the chemical composition, changing the knots' surface roughness,[30] or introducing stimulus-responsive molecules onto the spindle-knots.[31,32]

A typical example can be found in Figure 5, where joints of those A-SSs are all covered with smooth PMMA but the spindle-knots differ from one another.[30] Specially, the spindle-knots in Figure 5 are coated with (A) smooth PMMA, (B) smooth PS, (C) rough polyvinylidenefluoride (PVDF), and (D) smooth PVDF. When these A-SSs were placed in the same fog flow, interestingly, with the same smooth surface, the ones with PMMA spindle-knots and PS spindle-knots drive water droplets to move in reverse directions (Figure 5A, B); with the same PVDF covered, the ones with rough and smooth spindle-knots drive water droplets to move in opposite directions as well (Figure 5C, D). Inherently, the direction of water droplets on A-SSs is determined by the comprehensive forces arising from chemical gradient, Laplace pressure gradient, and contact angle hysteresis. Since sizes of the spindle-knots in the experiment are chosen to be the same, the Laplace pressure gradients inside the droplets are constant. The spindle-knots' chemical composition and roughness, or wettability, thus are key factors influencing the movement direction. Through tuning the spindle-knot's wettability, the movement direction of droplet on the A-SSs can be manipulated precisely.

In addition to this non-in-situ direction switch of a droplet moving on different spindle-knots, in situ direction switch of a droplet moving on the same one spindle-knot has also been achieved through introducing stimulus-responsive molecules onto the spindle-knots. Stimulus-responsive molecules are widely used to change a surface's wettability.[33,34] By modifying the spindle-knots with temperature sensitive copolymer poly(methyl methacrylate)-*b*-poly(*N*-isopropylacrylamide) (PMMA-*b*-PNIPAAm) and controlling the experimental temperature below and above the lower critical solution temperature (LCST) of PNIPAAm,[31] the direction of the water droplets' movement on the A-SSs can be reversed. In detail, a surface modified with PMMA-*b*-PNIPAAm is more wettable below the LCST and less wettable above the LCST due to the PNIPAAm configuration change below and above

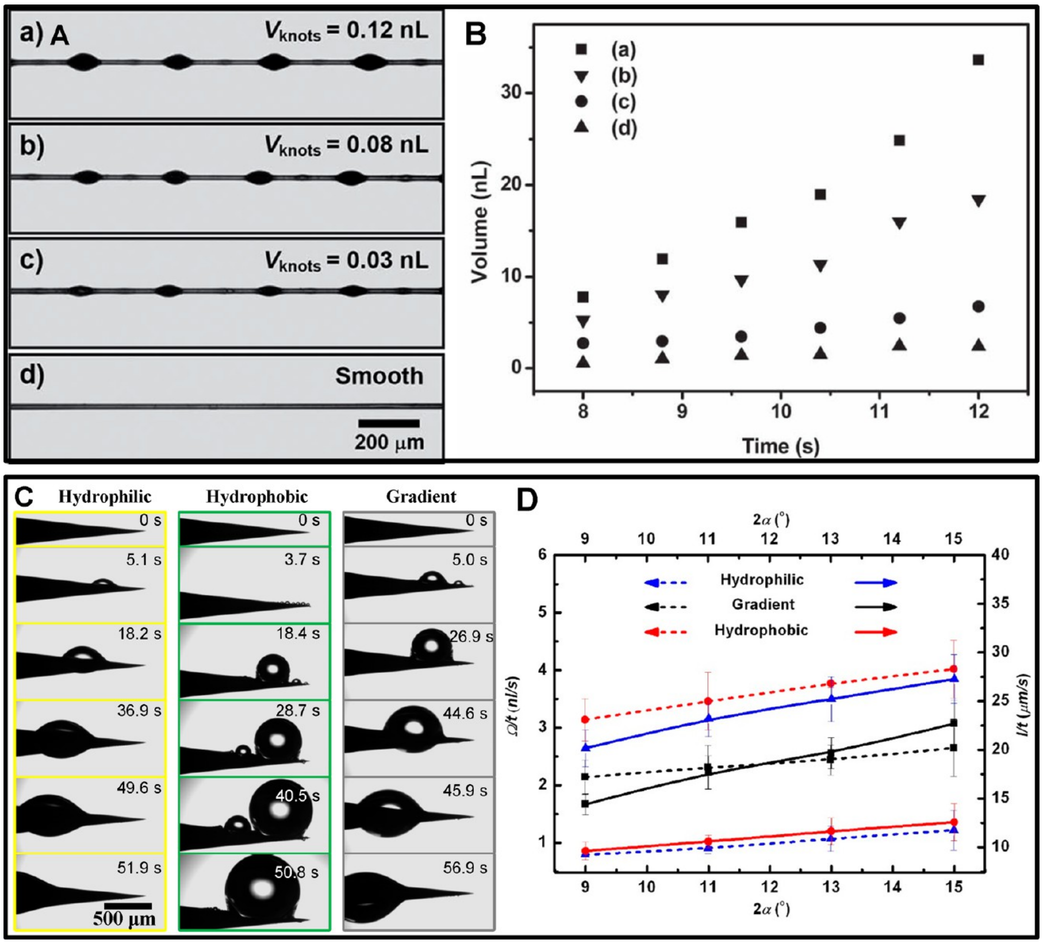

Figure 9. Directional water collection on the A-SSs and A-CSs. (A) Controlled fabrication of A-SSs with varied size of spindle-knots. The ones with larger spindle-knots collect more water at a fixed time (B). (C) Directional water collection on three kinds of A-CSs. Comparing with the A-CSs with purely hydrophilic and hydrophobic surface, the one with gradient wettability integrates both large water droplet growth rate and large droplet movement speed, realizing continuous and efficient fog collection (D).

the LCST ~ 32 °C (Figure 6A). This wettability change of the spindle-knot further induces change of the droplet's movement direction. As shown in Figure 6B and C, the A-SSs with PMMA-*b*-PNIPAAm spindle-knots drive water droplets toward the spindle-knot at 25 °C but away from the spindle-knot at 40 °C in the same humidity. Besides, a surface covered with photosensitive azobenzene polymer can transform from a less hydrophilic to hydrophilic state due to the molecular configuration transformation under UV and vis treatment (Figure 6D). This wettability change further induces inversion of the direction of droplet movement on A-SSs with azobenzene modified spindle-knots (Figure 6E, F).[32]

3.2. Directional Water Droplet Transport on A-SSs with Nonuniform Spindle-Knots

Bioinspired A-SSs with uniform spindle-knots that closely resemble structures of the natural spider silks not only can reproduce the natural spider silks' ability to transport water droplets toward the spindle-knots but also can manipulate droplets to move reversely. However, due to the limitation from periodicity,[10] droplets usually can only be transported between two uniform spindle-knots. Through constructing nonuniform spindle-knots, the long-distance transport can be achieved.[35,36] Figure 7A shows the directional transport of water droplets on the artificial spider silk with nonuniform spindle-knots produced from multiple dip-coating treatments.[35] Figure 7B gives a schematic illustration of this directional transport. The multilevel sized spindle-knots contain the main, the satellite, and the subsatellite spindle-knots. When the A-SS was placed in foggy atmosphere, water droplets deposited on it conducted directional movement from joints to spindle-knots and directional coalescence[37] from subsatellite spindle-knots to satellite spindle-knots and finally to the main spindle-knots (Figure 7B). Apart from the moving tendency from joints to spindle-knots, the gradually increasing capillary force from the subsatellite to the satellite to the main spindle-knot responses for this long-distance transport. Another kind of A-SS with nonuniform spindle-knots can be found in Figure 7C and D, where Figure 7C gives a sketch diagram of a tilted dip-coating method to prepare gradient spindle-knots, that is, the spindle-knots increases their size along a specific direction.[36] Comparing with the artificial spider silk in Figure 7A, the gradient spindle-knots can transport water droplets directionally in a much greater distance (Figure 7D). This relatively long-distance transport may make more sense in practical applications.

3.3. Directional Water Droplet Transport on A-CSs

As mentioned above, the cactus spine is capable of transporting liquid droplets consistently toward the base side, forming a natural long-distance directional liquid transport system.[11] Following the principle of cactus spines in transporting liquid droplets, we fabricated the A-CSs on both small and large scale, and demonstrated their ability to directionally transport water droplets in air[38] and oil droplets underwater.[39] Figure 8A shows the SEM image of a single A-CS prepared via gradient electrochemical corrosion followed by gradient chemical modification. The surface of the as-prepared A-CS is covered by homogeneous nanostructures (Figure 8B). Placing it under a fog flow, a water droplet deposited on it can be transported directionally from the tip to the base side with increasing volume.[38] When this A-CS is moved underwater and sprayed with an oil/water mixture, the oil droplet deposited on it can be transported directionally to the base of the A-CS, just as the behavior of water droplets in air (Figure 8D).[39] For the convenience of large-scale fabrication, we developed a method combining mechanical lithography and mold replica technology to prepare array of A-CSs; see SEM image in Figure 8C. The inset shows ridged structures on the arrayed A-CSs. Detailed discussion about the directional oil droplet transport will be given in the next part.

4. DIRECTIONAL LIQUID TRANSPORT RELATED APPLICATIONS

Directional liquid transport on 1D materials can find vast applications,[40] such as efficient fog collection,[41] microsized oil/water separation,[39] filtering and smog removal,[42] and drug delivery.[43] In this part, we will mainly introduce some related applications from the aspect of fog collection and oil/water separation.

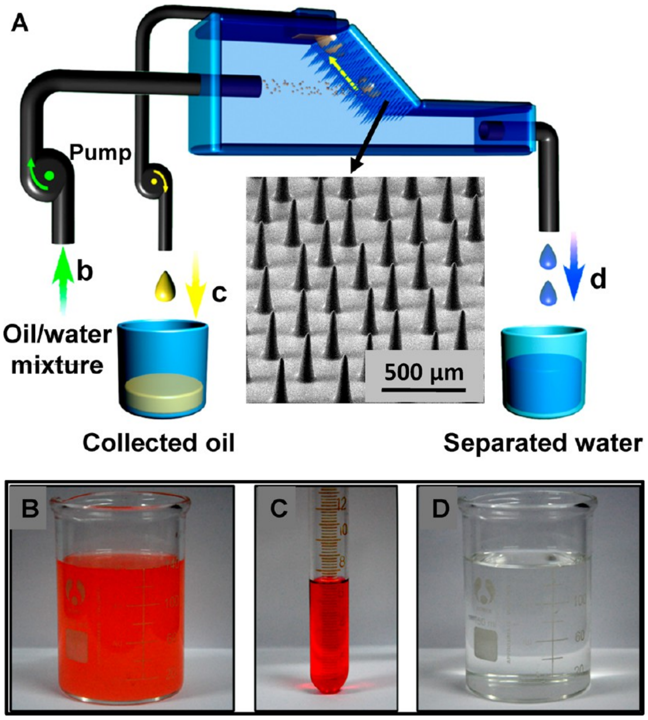

Figure 10. Oil/water separation of arrayed A-CSs based on directional oil droplet transport under water. Setup for oil/water separation (A) and demonstration of its oil/water separation ability showing (B) the oil/water mixture before separation, (C) the oil collected, and (D) the water separated. The SEM image in the middle shows the array of A-CSs used.

4.1. Fog Collection

Fog, as a potential water resource, has long been exploited to feedwater supply utilizing various kinds of fog collectors. However, both the traditional mesh-based fog collectors[44] and the newly appeared 2D solid fog collectors[45−47] with patterned hydrophobic and hydrophilic surfaces bear the same drawbacks: the water droplets collected depart behind time. Because water droplets can only depart from the collector's surface on the condition that their growing weight is large enough to overcome the resistance force. This relatively slow refreshing rate of the collector surface counts against the efficient fog collection.[40] Inspired by the directional transport of water droplet on the natural spider silks and cactus spines, we designed fibers resembling structures of spider silks and cactus spines to collect water droplets from fog. The fog collection ability of these 1D structures demonstrates striking increase. First, A-SSs with varied size of spindle-knots (Figure 9A) were prepared.[48] These A-SSs show distinct water collection ability at the same fog flow condition: the larger the spindle-knots, the more water they collected at the same time (Figure 9B). This outcome can be interpreted from two aspects: the larger spindle-knots increase area for fog collection; more important, the larger spindle-knots provide more driving force and water droplets can be transport directionally more efficiently, freeing the original place for next cycle with faster pace. Figure 9C shows the directional water collection on A-CSs, conical copper wires, with different wettability.[38] Comparing with hydrophilic conical copper wire with large droplet motion speed but small droplet growth rate and hydrophobic conical copper wire with large droplet growth rate but small droplet motion speed, the conical copper wire with gradient wettability shows superiority of both large water transport speed and large water collecting velocity (Figure 9D). This balance of droplet motion speed and droplet growth rate is critically important to efficient fog collection. This cactus-spine-inspired dual-gradient design therefore favors the efficient fog collection.

4.2. Microsized Oil/Water Separation

Materials capable of separating oil/water mixture are highly desirable due to the frequent oil spill accidents and increasing discharge of industrial oily wastewater worldwide. Traditional membrane-based separating materials, such as oil-removing[49] and water-removing materials,[50] and bulk absorbing materials,[51] have played a big role in treating macrosized oil/water mixtures. Recently, Tuteja et al. has developed a kind of hygro-responsive membrane,[52] able to separate a range of different oil/water mixtures in a single-unit operation with high separation efficiency. However, these above-mentioned methods are limited either by easily fouling or by difficulty in post-processing. What is more, they all bare a common disadvantage that they are unable to treat the microsized oil/water mixture with high throughput.

Inspired by the directional water collection on cactus, a novel "artificial cactus under water" was developed to directionally collect microsized oil droplets from oil/water mixtures effectively.[39] Figure 10A depicts the sketch map of a typical experimental setup, with arrays of A-CSs fixed downward-sloping at an appropriate angle. Under sustained spray of oil/water mixture, tiny oil droplets deposited on the surface of the A-CS increase their volume and move toward the region with larger curvature radius as soon as a critical volume is reached. In this manner, tiny oil droplets are extracted from the oil/water mixture and oil/water separation is fulfilled. Figure 10B−D displays the oil/water mixture, pure oil collected, and pure water separated, respectively. This directional oil droplet collection design is free of blocking and can support high throughput. In addition, for convenience of scaled preparation, the classic soft seal polydimmethylsiloxane (PDMS) was exploited to fabricate the A-CSs. As the intrinsic lipophilicity of PDMS, the A-CSs can collect oil by virtue of the interfacial interaction between PDMS cones and the oil droplets without aid from an external power supply, which is otherwise difficult to implement. This cactus-spine-inspired cone-structured material therefore has even broader applications in microsized oil collection with high continuity and high throughput.

■ CONCLUSION AND OUTLOOK

This Account reviews recent progress on bioinspired 1D materials for directional liquid transport, from directional liquid transport on 1D natural materials to that on 1D artificial materials. Specifically, based on studies of directional liquid transport on natural spider silk and natural cactus spine (Figure 11A), directional transport of water droplets on A-SSs (Figure 11B), tunable transport on A-SSs with uniform spindle-knots (Figure 11C), integrated transport on A-SSs with nonuniform spindle-knots (Figure 11D), and directional transport of liquid droplets on a single A-CS (Figure 11E) and arrayed A-CSs potential for fog collection (Figure 11F) and oil/water separation (Figure 11G) are summarized.

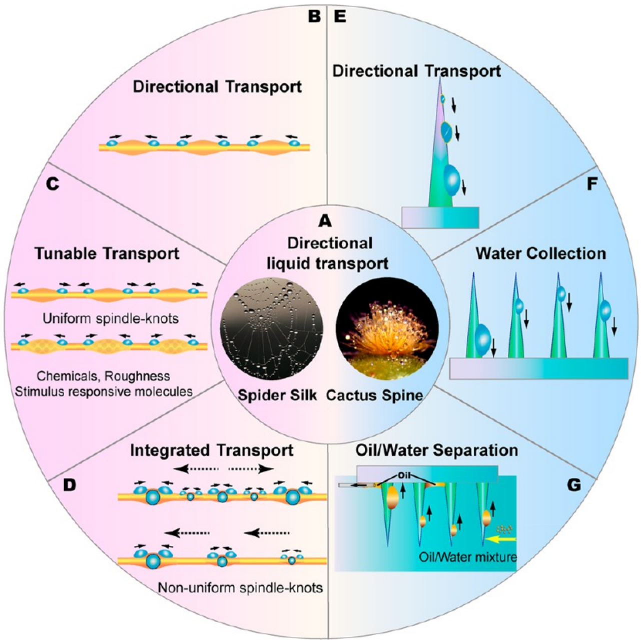

Figure 11. Schematic illustration of the designing principles and applications of natural spider silk and natural cactus spine (A) inspired 1D materials for directional liquid transport. Through various strategies, A-SSs with uniform spindle-knots capable of transporting water droplets toward knots can be obtained (B). By changing the chemical composition or surface roughness of spindle-knots or by introducing stimulus-responsive molecules onto the spindle-knots, the transport direction of water droplets can be tuned (C). Taking advantage of the multilevel and gradient spindle-knots on the A-SSs, the integrated transport can be achieved (D). (E) Directional transport of water droplets on the A-CSs. Scaling the A-CSs into array, they can be used to efficiently collect water in air (F) and collect oil under water, realizing oil/water separation (G).

Research of 1D materials for directional liquid transport is just beginning. There are numerous challenges and opportunities ahead of its development. First, since nature always gives us clues to design materials with unique properties, more sorts of living organisms with 1D directional liquid transport systems wait to be discovered. Second, stimulus-responsive molecules are effective in controlling surface's wettability, so other kinds of stimulus-responsive molecules even multiple-responsive molecules should be incorporated into 1D materials for directional liquid transport. Finally, more applications related to the directional liquid transport of 1D materials, such as delivery of drugs, removal of smog and microfluidics, deserve exploitation in depth. In the future, we will continue our research on the above aspects, with particular focus on bioinspired design of smart material system.

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Notes

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