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Photo-controlled water gathering on bio-inspired fibers†

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We report photo-controlled water gathering on bio-inspired fibers. We have designed a bio-inspired fiber using azobenzene (Azo) polymer materials, with roughness and a curvature similar to the spindle-knots of wetted spider silk. We demonstrate that the cooperation between roughness and curvature and the photo-responsive wettability play a key role in water gathering after Vis or UV irradiation, which regulate effectively the separation of water droplets away from the spindle-knots or the coalescence towards the spindle-knots, respectively. This study offers an insight into the design of novel gradient surfaces that may drive tiny droplets to move in as-desired directions, which could potentially be extended to the realms of fluid-control in micro-scale engines, sub-micron masks, heat transfer, water-collecting devices and systems.

The manipulation of droplets on surfaces is an important issue in many engineering applications such as microfluidics and integrated DNA analysis devices,[1,2] fog harvesting,[3] filtration,[4] and condensers.[5] Although a gradient in the surface tension has been used to induce a net mass transport of liquids, usually a low hysteresis must be prepared. Recently, multi-gradient force cooperation as a quick, easy, cheap and effective method, has attracted a lot of attention.[6] For example, desert beetles use micrometre-sized patterns of hydrophobic and hydrophilic regions on their backs to capture water from humid air.[2] Spider silk can collect directionally water from humid air, relying completely on multi-structures of spindle-knots and joints on wetted spider silk, generating a cooperation between the surface energy gradient and the curvature gradient.[3] However, directional water gathering on their surface is only uni-directional and can not be controlled reversibly.[7–12] Up to now, it remains a great challenge to regulate effectively the dynamics of droplets on surfaces, especially, to control the directional motion of tiny droplets on a surface at one-dimension level, *e.g.*, on fibers.[13–15]

In this communication, and inspired by the concept of gradient cooperation on wetted spider silk,[3,16] we have designed a kind of smart fiber using an azobenzene (Azo) polymer, similar to the spindle-knots of wetted spider silk (Fig. 1). A wettability gradient on the spindle-knots was formed and also controlled *via* reversible *trans* and *cis* photo-isomerization of the Azo group, and thus the driving force for tiny droplets could be tuned reversibly in opposite directions along the spindle-knots of the fiber. The results demonstrate the cooperation between gradients of roughness, curvature, and wettability on one-dimension fiber materials that modulate water gathering in opposite directions by Vis and UV irradiation. This study offers a novel insight into the design of novel gradient surfaces that may control the motion of droplets in different directions. This could potentially be extended into the realm of micro-scale engines, sub-micron masks, heat transfer, and water-collecting devices.[16–18]

Bio-inspired fibers can be fabricated by using a P(MMA-Azo) polymer *via* coating polymer methods.[19] To obtain a smart fiber on which tiny droplets can be driven controllably, we considered that multi-gradients need to be fabricated onto the surface, just as in wetted spider silk. Meanwhile, the wettability of the surface can be modulated by external stimuli. As known, a block copolymer (BCP) can self-assemble into microphase separation nanostructures and the blocks in the nanodomain exhibit their own properties independently and also affect each other, which provides a great advantage for the design of smart interfaces. An Azo polymer is a kind of photo-responsive polymer, where photoisomerization of the azo group would cause reversible changes in the surface wettability.[9] In addition, poly(methylmethacrylate) (PMMA) is very suited to fabricate these special structures[3] and has a high glass transition temperature

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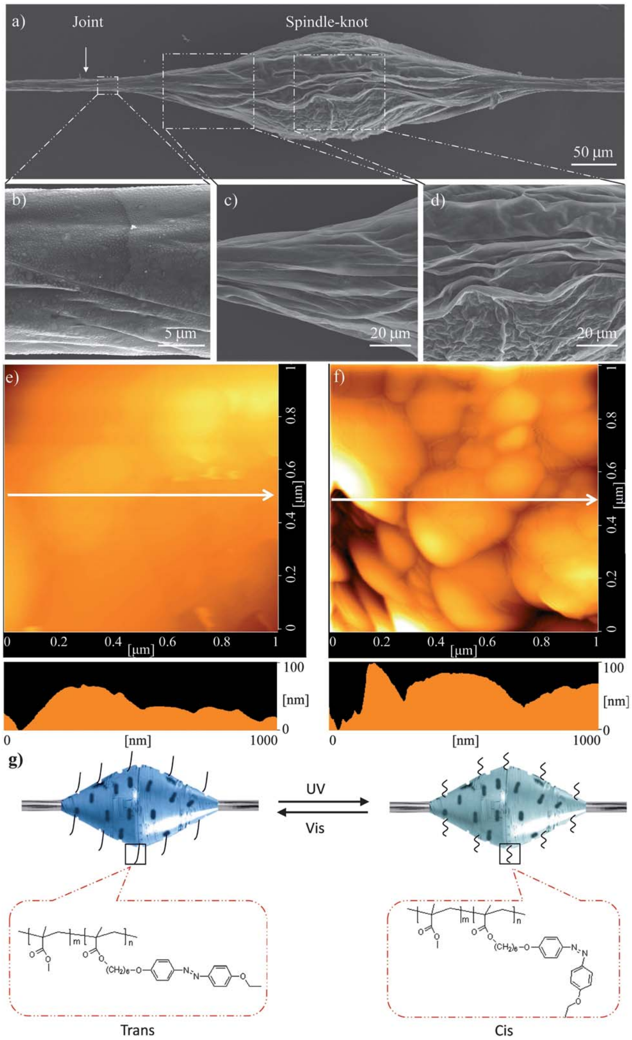

Fig. 1 SEM images of a spindle knot on a fiber. (a) The spindle-knot and joint of a fiber. (b–f) Morphology images: the joint has a relatively smooth surface (b); the side of the spindle-knot (c) is less rough than the centre of the spindle-knot (d); and (e and f) AFM images corresponding to (c) and (d). The gradients of roughness and curvature can be formed along the fiber from a spindle-knot to a joint. (g) Illustration of the reversible photo-controlled *trans* and *cis* isomers of the Azo polymer on the bio-inspired fiber surface with a roughness gradient.

to act as the physical crosslink of Azo. Therefore, a block copolymer, consisting of PMMA and the Azo unit, was synthesized *via* the typical Atom Transfer Radical Polymerization (ATRP) method (denoted as P(MMA-Azo)) (Fig. S1†). It has been demonstrated that P(MMA-Azo) has excellent photo-responsive characteristics, *e.g.*, the nano-level roughness by atomic force microscopy (AFM) (Fig. S2a and b†). The root-mean-square (RMS) roughness was obtained by AFM analysis. The RMS roughness for the smooth surface is 0.73 nm after Vis irradiation and 0.92 nm after UV irradiation. The increase in the surface roughness after UV irradiation may be due to a free-standing *trans* molecule changing to a shorter and wider *cis* molecule, and so photoisomerization gives rise to an increase in the cross-sectional area of Azo.[20] Due to the photo-controlled change in the dipole moment of the Azo unit upon *trans* to *cis* isomerization,[21,22] a reversible wettability change is also observed (Fig. S2c and d†). The enhancing effect of the roughness on the wettability is also seen in Table S1.† Thus, we have ensured that the desired bio-inspired fiber can be achieved successfully.

To examine the effect of the gradients on tiny droplets on the fiber for water gathering, fog flowing *via* an ultrasonic humidifier was introduced into a sample chamber, instead of using a flow against the surface of the fiber.[9,23,24] The behaviour of tiny droplets on the surface of the spindle-knots on the fiber was observed and recorded with a charge coupled device (CCD) camera over a period of time, as shown in Fig. 2. Firstly, we observe the behaviour of droplets on the fiber after Vis irradiation. Initially, tiny water droplets are gathered randomly on the surface of the spindle-knot, and then, as the droplets grow in a period of 20–500 s, one side of the droplets extends to the joint. The whole droplets tend to move away from the spindle-knot (Fig. 2a). In contrast, after UV irradiation, the tiny droplets

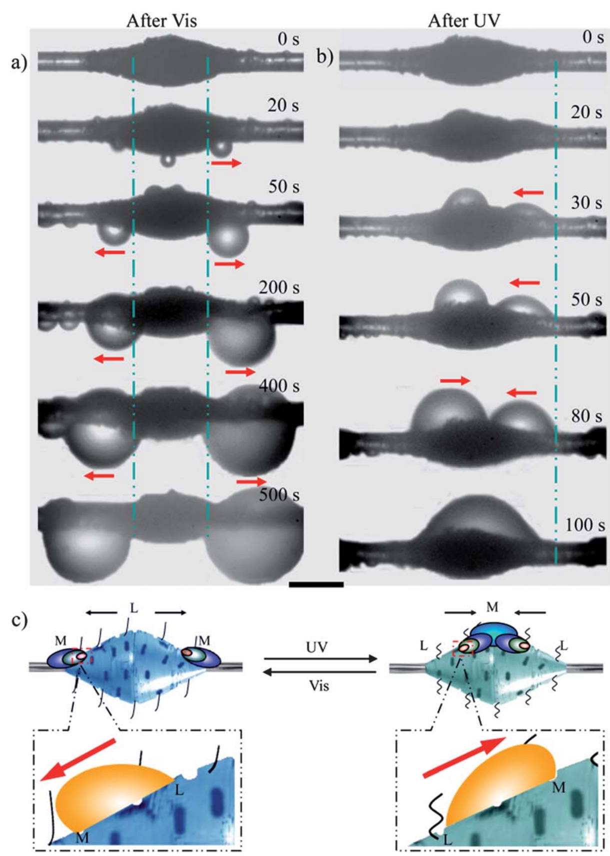

Fig. 2 *In situ* optical observation of directional water gathering on a bio-inspired fiber: (a) after Vis irradiation, one side of the droplet moves towards the joint and away from the spindle-knot in a period of 0–500 s (indicated with red arrows). (b) After UV irradiation, one side of the droplet moves towards the centre of the spindle-knot and finally, the droplet coalesces with another droplet at ~100 s. Scale bar is 50 µm. (c) Illustration of tiny droplet directional gathering *via* control of the wettability gradient. A tiny gathered droplet would be pinned on the surface and its growth causes the CAs to increase continuously. When θ_M reaches θ_{aM}, edge M would be driven to the more wettable side (M and L correspond to more and less wettable sides, respectively). Insets indicate the tendency of the initial gathered droplets to move, the arrows indicate the direction of movement.

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display the opposite behaviour. The tiny droplets extend directionally to the spindle-knot with ease, coalescing with others on the spindle-knot (Fig. 2b) in a short time of ~100 s. It is obvious that after UV irradiation, the expanding velocity of the droplet is larger than that after Vis irradiation. This may be due to the fact that after UV irradiation, the polymer exhibits hydrophilicity and droplets can be easily captured by the fiber. This observation implies that UV irradiation provides the bio-inspired fiber with the water gathering ability.

In order to thoroughly understand the unique phenomenon, we have analyzed the forces exerted on the water droplets. There are three forces: *i.e.*, the wettability gradient force (F_W), the hysteresis force (F_H) and the Laplace force (F_L),[16] which result from the roughness gradient and the photo-responsive wettability, contact angle (CA) hysteresis and curvature gradient, respectively. As it is well known, a wettability gradient on a surface can arise from differences in either the surface chemical composition or the surface roughness, which would drive the water droplets towards the more wettable region of the surface.[16] In our experiment, the surface of the bio-inspired fiber is completely coated by BCP (Fig. 1) and the chemical composition is identical. In addition, the rough nanostructures on the centre of the spindle-knots and relatively smooth structures on the end of the spindle-knots create a roughness gradient along the fiber (Fig. 1b–f) (the RMS roughness is 7.48 nm on the centre and 4.60 nm on the end). According to Wenzel's equation, roughness makes a surface more wettable when it is hydrophilic and less wettable when hydrophobic. As mentioned above, the polymer surface is hydrophobic after Vis irradiation and hydrophilic after UV irradiation, respectively. The roughness gradient along the fiber would bring hydrophilic–hydrophobic-wettable gradient forces (F_W) acting on opposite sides of the droplet, which moves away from spindle-knots after Vis irradiation and towards spindle-knots after UV irradiation. The hysteresis force (F_H) is related to the CA hysteresis, in opposition to the movement direction, which usually blocks the movement of droplets.[25,26] The Laplace force (F_L) arises from the curvature gradient of the spindle-knots, which points to the centre of the spindle-knots.[16] Therefore, the direction-controlled water gathering behaviour could be explained by the cooperation of multi-gradients after Vis or UV irradiation. Due to the high hysteresis (F_H) (Table S1†), initially, when a tiny droplet is gathered on the surface of the bio-inspired fiber, the droplet exhibits an asymmetric shape with unequal CAs at edges M and L (the CA on the M side is larger than that on the L side, the M and L correspond to "more wettable" and "less wettable" side),[19] as illustrated in Fig. 2c, and grows by the continuous condensation of fog steam. Condensation causes the continuous increase of the CAs at M and L. When the dynamic CA (θ_M) at M reaches the advancing CA, θ_{aM}, edge M moves to the more wettable side (surface energy minimum principle). According to the direction of the wettability gradient, the droplets would grow away from or towards the spindle-knots after Vis or UV irradiation, which is consistent with our observations.

To compare the ability to gather water after Vis and UV irradiation, droplet size as a function of time is shown in Fig. 3.

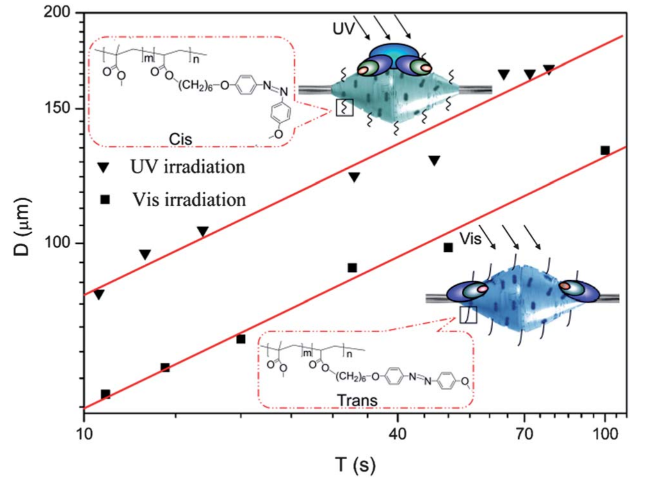

Fig. 3 Relationship between the diameter of condensation droplets (*D*) and condensation time (*T*). After Vis irradiation, there is a linear relationship given by $\lg D_{Vis} = 0.444 + 0.337 \lg T$. After UV irradiation, there is a linear relationship given by $\lg D_{UV} = 0.617 + 0.320 \lg T$. At a given *T*, $D_{UV} > D_{Vis}$, indicating a higher efficiency in water gathering on the bio-inspired fibers after UV irradiation.

In general, droplet growth follows a power law with time:[7,8] *i.e.*, $D = aT^{\mu}$ (or $\lg D = \mu \lg T + A$, where A is constant), where D is the droplet diameter, a is a coefficient, T is the condensation time and μ is an exponent. For water droplets on silanized glass and silicon surface, $\mu \sim 1/3$ and 0.23, respectively.[9,10] If there is coalescence, $\mu \sim 1$.[11] Based on our experiment data, there seems to be a linear relation between these lg D and lg T: *i.e.*, after Vis irradiation, $\lg D_{Vis} = 0.444 + 0.337 \lg T$ and after UV irradiation, $\lg D_{UV} = 0.617 + 0.320 \lg T$. It is inferred that in a given observed time T, $D_{UV} > D_{Vis}$. The reason may be as follows: after Vis irradiation, the direction of F_L is opposite to that of F_W and the motion of edge M away from the spindle-knots would be blocked. In contrast, after UV irradiation, the direction of F_L and F_W is the same and the hysteresis force is low (Table S1†), so the edge M would be driven more powerfully to spread along the spindle-knots and the water drop would have a larger surface area to capture droplets from the surroundings. Another reason may be the fact that the more hydrophilic fiber would capture droplets more easily. Therefore, in the whole water gathering process, the bio-inspired fiber after UV irradiation displays an excellent water gathering efficiency.

Conclusions

In conclusion, we report a photo-controlled effect on water gathering in bio-inspired fibers composed of Azo polymer, with roughness and curvature gradients similar to the spindle-knots of wetted spider silk. We demonstrate that the cooperation between roughness and curvature and the photo-responsive wettability play a role on the bio-inspired fibers after Vis or UV irradiation, which regulate effectively the water droplets to separate away from the spindle-knots or coalesce toward the spindle-knots, respectively. This study offers an insight into the design of novel gradient surfaces that may drive tiny droplets to move in as-desired directions, which could potentially be

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extended to the realms of in micro-scale engines, heat transfer and water-collecting devices.

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