Supplementary Information:

Temperature-triggered directional motion of tiny water droplets on bioinspired fibers in humidity

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Experimental section:

Synthesis and thermal responsiveness of PMMA-b-PNIPAAm: Block copolymers of PMMA-b-PNIPAAm were obtained by Atom Transfer Radical Polymerization (ATRP) method. The Gel Permeation Chromatography (GPC) measurement was employed to confirm the structures of the copolymers. Water contact angles were measured with an OCA20 machine (Dataphysics Instruments GmbH, Germany). The PMMA-b-PNIPAAm rough film was made by dripping PMMA-b-PNIPAAm/(DMF+ethanol) solution (DMF: N,N-dimethylformamide) (1:10:1, PMMA-b-PNIPAAm: DMF: ethanol, by weight) on a clean silicon substrate. After the solvent volatilization in the given condition (Temperature: 25 ^{o}C, Humidity: 75%), the film was formed. This method is same to that of bioinspired fiber preparation. A temperature-responsive wettability may be dominated by surface chemistry, i.e., a conformational change of the NIPAAm molecular chain at different temperatures: at 25 ^{o}C (< LCST), C=O and N-H groups in PNIPAAm form inter-molecular hydrogen bonds with water molecules and the film is hydrophilic. On the contrary, at 40 ^{o}C (>LCST), C=O and N-H groups form intra-molecular hydrogen bonds, leading to a dehydrated, collapsed state and the film exhibits hydrophobicity (Fig. 1). The thermal responsiveness of PMMA-b-PNIPAAm film is sensitive and the water contact angles (CAs) can be changed from 51.64^{o} to 107.09^{o} with the temperature from 20 ^{o}C to 45 ^{o}C. Advancing and receding CA data of PMMA-b-PNIPAAm film indicate the contrasting CA hysteresis on the surfaces between 20 ^{o}C or 45 ^{o}C (e.g., 43^{o} at 20 ^{o}C; 60^{o} at 45 ^{o}C) (Fig. S2). Atomic force microscopy (AFM) images under water show the change of roughness at nano-level with temperatures (Fig. S2).

Fabrication of bioinspired fibers: Due to a number of advantageous characteristics, such as high strength, high toughness, good electrical and thermal conductivity, and light weight, carbon fibers were chosen to fabricate bioinspired fiber. In order to improve the interfacial adhesion between the fibers and polymer matrices, carbon fibers were firstly treated by low temperature plasma to increase the surface roughness. The carbon fiber specimen was made by using an adhesive tape to fix a single carbon fiber (obtained from Institute of Coal Chemistry, Chinese Academy of Sciences, China) on a U-shaped holder with a certain amount of tension and the length of the fiber was about 2.5 cm. Bioinspired fibers with PMMA-b-PNIPAAm spindle-knots were prepared by immersing carbon fiber specimens in the PMMA-b-PNIPAAm/(DMF+ethanol) solution (DMF: N,N-dimethylformamide) (1:10:1, PMMA-b-PNIPAAm: DMF: ethanol, by weight) and drawing it out horizontally at different velocities (50~150 mm s^{-1}). A cylindrical film of polymer solution was then formed on the fiber surface and spontaneously broken up into polymer droplets along the fiber owing to the Rayleigh instability. After the fiber was dried completely in the given condition (Temperature: 25 ^{o}C, Humidity: 75%), periodic polymer spindle-knots formed. The surface roughness gradient of the spindle-knots was also designed through phase separation induced by the solvent component in the polymer solution.

Characterization of microstructure: The structures of fiber and spindle-knot were observed by scanning electron microscope (SEM, Quanta FEG 250, FEI, America) at 25 kV with gold plating. AFM experiments were performed using an Agilent AFM series 5500 (Agilent Technologies). Imaging was carried out in the AAC mode. The cantilevers (Nanosensor) used have frequencies within of 204–497 kHz and force constant values 10–130 N/m.

Experiments on motion of tiny water droplets: In order to clearly observe the motion of water droplets, the bioinspired fibers placed on a small U-shaped holder were put in a chamber of sample. Numerous small water droplets generated by an YC-E350 ultrasonic humidifier (Beijing YADU Science and Technology Co., Ltd., China) were introduced into the sample chamber. The behavior of

water droplets was recorded by the optical contact angle meter system (OCA40Micro, Dataphysics Instruments GmbH, Germany) with time scale.

Supplementary Figure Legend: Fig. S1-S3

Fig. S1:

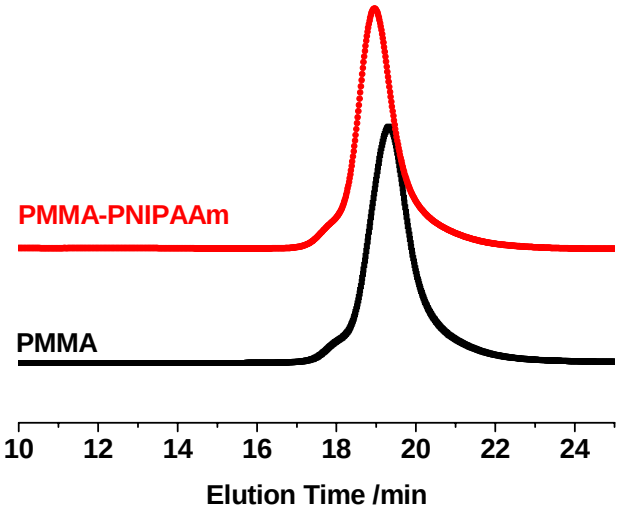

Fig. S1 The GPC curves of the original PMMA macroinitiator and block copolymer PMMA-b-PNIPAAm. Compared to the starting PMMA macroinitiator, a visible unimodal shift to higher molecular weight is seen in the figure, which indicates that NIPAAm is successfully introduced into PMMA. Number-average molecular weight (M_n) of PMMA-b-PNIPAAm block copolymer is 46,400 and the polydispersity index (PDI) is 1.16.

Fig. S2:

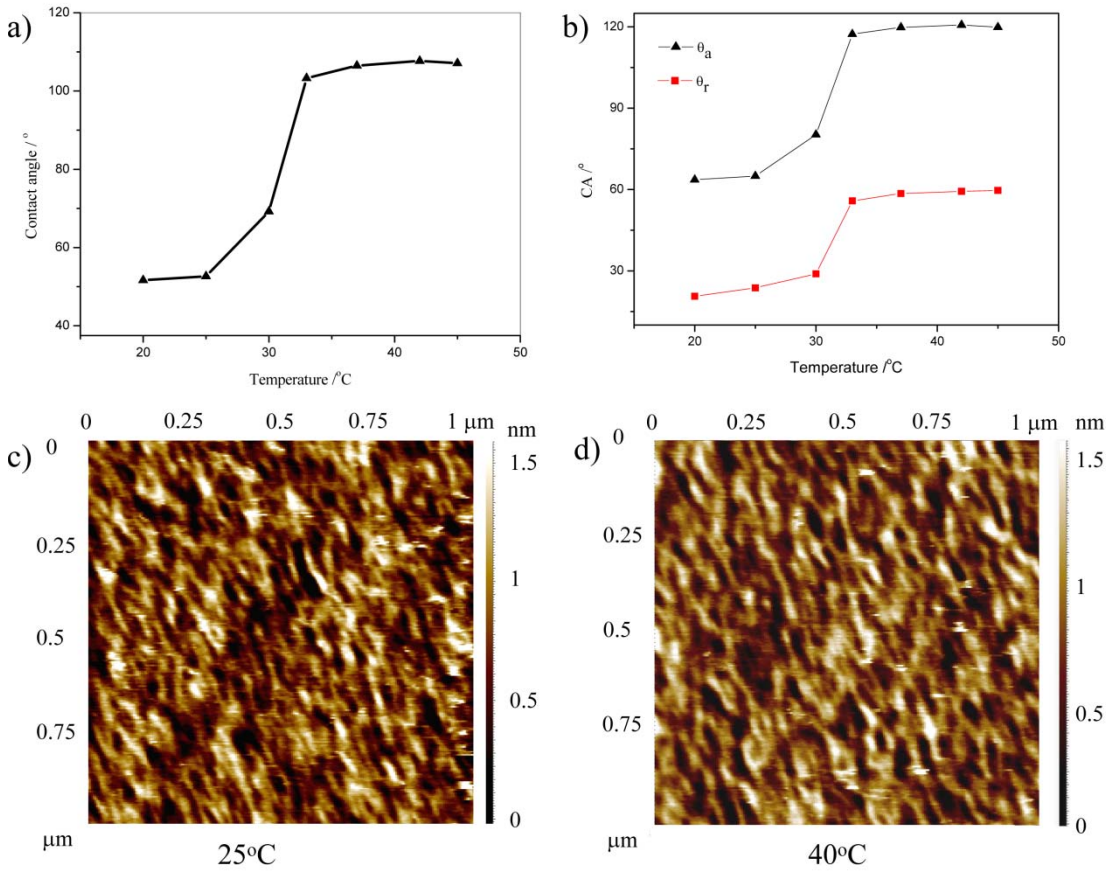

Fig. S2 a) Temperature dependences of water CAs for PMMA-b-PNIPAAm rough surface film. When the temperature increases from 20 °C to 45 °C, the CA of a 2 μl water droplet changes from 51.64° to 104.82°. It is proposed that such a surface wettability change corresponds to a discontinuous conformational change of the NIPAAm polymer at LCST. b) Advancing (black) and receding (red) CA data of rough PMMA-b-PNIPAAm film. It indicates that on rough surface, the CA hysteresis is as large as more than 40°. AFM images of film under water c) at 25 °C and d) 40 °C, indicating a nano-level change of roughness.

Fig. S3:

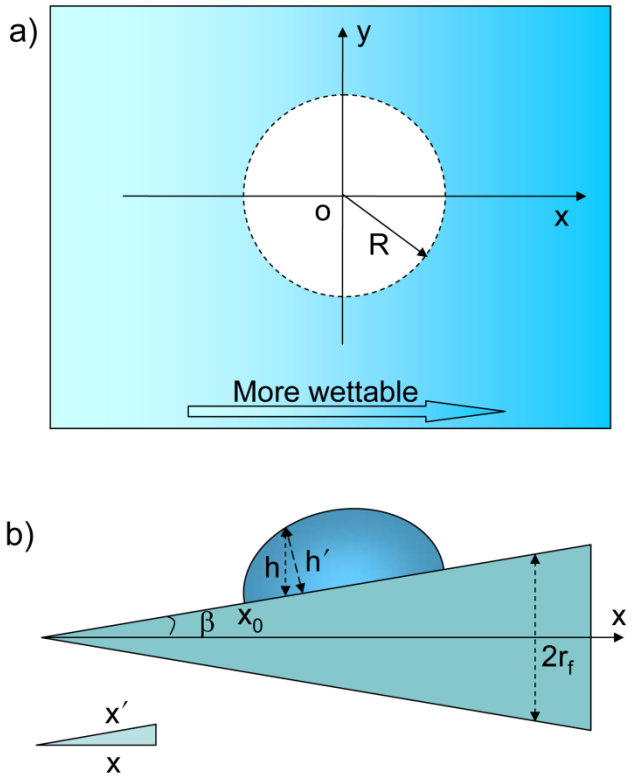

Fig. S3 Plan view of the footprint of the water droplet sited on the wettability gradient surface. Wettability gradient force (F_W) acting on the opposite sides of the droplet edge, and points to spindle-knot at low temperature (25 ^oC) and to joints at high temperature (40 ^oC), which is described as:

$$F_W = \pi R^2 \gamma (\frac{d\cos\theta}{dx})$$

Here R is the base radius of the droplet, γ is the surface tension of water, θ are the position-responsive sessile CA of the water droplet on the fiber surface and dx is the integrating variable along the fiber axis. Hysteresis force (F_H) due to CA hysteresis, which is always opposite to the moving direction, blocks the moving of the droplets. The magnitude of hysteresis force is described as:

$$F_H = 2R\gamma\ (\cos\theta_{ro} - \cos\theta_{ao})$$

Where θ_{ro} and θ_{ao} are the position-dependent receding, advancing CAs at the central line of the drop on the solid surface, respectively. b) Estimation of Laplace force (F_L) induced by curvature gradient when a droplet is in the 'clamshell' shape. The force points to center of spindle-knot and can be represented as:

$$F_L = \pi\gamma \sin\beta \int_{x_0}^{x_0+2R\cos\beta} \frac{h^2}{(r_f+R)^2} dx$$

Here γ is the surface tension of water, R is the base radius of the droplet, β is the half apex-angle of the spindle-knot, r_f is the local radius of the spindle-knot, h is the height of droplet, x_o is the position of water droplet, and dx is the integrating variable along the fiber axis. In order to deduce a simplified approximate formula to estimate the motion behavior of water droplet, considering that the spindle-knots used in the experiments were fabricated via same method, wettability gradient could be seen as a constant and F_W and F_H could be written as function of the radius of water droplet (R), i.e. F_W (R) and F_H (R). Compared to the final size of water droplet (R), r_f is small in size and it could be ignored to further simplify express equation of Laplace force (F_L) as follows:

$$F_L \approx \frac{\pi\gamma\sin\beta}{R^2}\int_{x_0}^{x_0+2R\cos\beta} h^2 dx = \frac{\pi\gamma\sin\beta}{R^2\cos^2\beta}\int_{x_0}^{x_0+2R\cos\beta} h'^2 dx = \frac{\pi\gamma tg\beta}{R^2}\int_{x_0}^{x_0+2R}\frac{\pi h'^2}{2}dx' = \frac{4}{3}\pi R\gamma tg\beta$$

where $h=\frac{h'}{\cos\beta}$, $x=x'\cos\beta$ and $\int_{x_0}^{x_0+2R}\frac{\pi h'}{2}dx'$ is the volume of water droplet, as shown in Fig. 4b. When temperature is above LCST, the total force (F_{Total}) can be described as:

$$F_{Total} = F_W - F_H - F_L \approx F_W(R) - F_H(R) - \frac{4}{3}\pi R\gamma tg\beta$$