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Biomimetic "Water Strider Leg" with Highly Refined Nanogroove Structure and Remarkable Water-Repellent Performance

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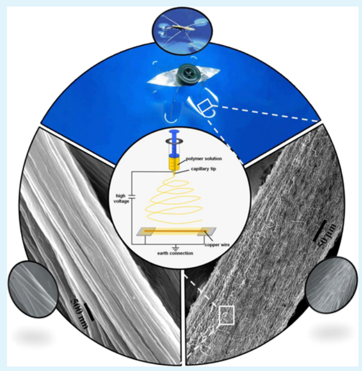
Supporting Information

ABSTRACT: The water strider is a wonderful case that we can learn from nature to understand how to stride on the water surface. Inspired by the unique hierarchical micro/nanostructure of the water strider leg, in this article, we designed and fabricated an artificial strider leg with refined nanogroove structure by using an electrospinning and sacrificial template method. A model water strider that was equipped with four artificial legs showed remarkable water-repellent performance; namely, it could carry a load that was about 7 times heavier than its own weight. Characterization demonstrated that, even though the artificial leg did not possess a superhydrophobic surface, the numerous nanogrooves could still provide a huge supporting force for the man-made model strider. This work enlightens the development of artificial water-walking devices for exploring and monitoring the surface of water. Because of the advances of the applied materials, the devices may fulfill tasks in a harsh aquatic environment.



KEYWORDS: *biomimetic, electrospinning, water strider leg, nanogroove surface, water-repellent performance*

INTRODUCTION

Walking on a water surface is always a beautiful and fantastic dream for human beings, whereas for water striders, it is a rather common scene. The water strider is a kind of common insect that lives in ponds and brooks. It has a remarkable ability to stand, walk, and even leap on a water surface effortlessly.[1−3] Original studies about the physical mechanism have revealed that the force to support the water strider is mainly composed of three parts: the buoyancy force, the curvature force, and the deformation force.[4] The locomotion of the water strider originated from the momentum of the swirling vortices beneath the water surface, like an oar.[5,6] Also, chemical scientists have further studied the water strider and found that the excellent water-walking ability derived from the superior water repellency of the strider legs, which possessed thousands of tiny setae with fine nanogroove structures.[7] These setae and nanogrooves can trap plentiful air bubbles under the water and provide a strong supporting force for the water strider to stand/run on a water surface.[8−10]

Investigating this unique water-proof performance and mimicking the water strider leg have attracted much attention.[11−15] It can be helpful to develop some water-standing/walking microdevices, which will have potential applications in exploring and monitoring activities on the water surface.[16−21] Shi's group has combined a layer-by-layer assembling technique with electrochemical deposition of gold aggregates to mimick the legs of water striders.[22] Meanwhile, they have demonstrated that the superhydrophobic coating could not only support their bodies on a water surface but also decrease the fluidic drag.[23] Furthermore, a kind of model water strider leg with a self-assembled coating of organic semiconductor nanowires has been fabricated by Jiang et al. via a new facile and low-cost approach.[24] Also, engineers even have equipped a micromotor on the superhydrophobic model strider legs to allow them to be self-driven.[25−30] However, to the best of our knowledge, the above reports always focused on how to obtain a superhydrophobic surface and ignored the similarity of the surface micro/nanostructures of water strider legs. Here, we consider that nanogroove structure may play a more important role in the remarkable water-repellent performance. Hence, we designed and fabricated a "water strider leg" with refined nanogrooves to verify the assumption.

Electrospinning (ES) is a facile and effective technique to build and control hierarchical micro/nanostructure.[31−35] Also, we expected to use it to mimick the surface structure of a water strider leg. Among the numerous ES materials, polyimide (PI) is a kind of high-performance polymer, especially in thermal stability and mechanical strength.[36,37] In this article, by using ES and a sacrificial template method, we have designed and fabricated an artificial strider leg with refined nanogroove structure that possessed excellent water-repellent performance and great thermal stability. Even without a superhydrophobic state, the artificial leg could still possess a huge supporting force. It would be helpful to develop these aquatic devices for exploring and monitoring the harsh environment.

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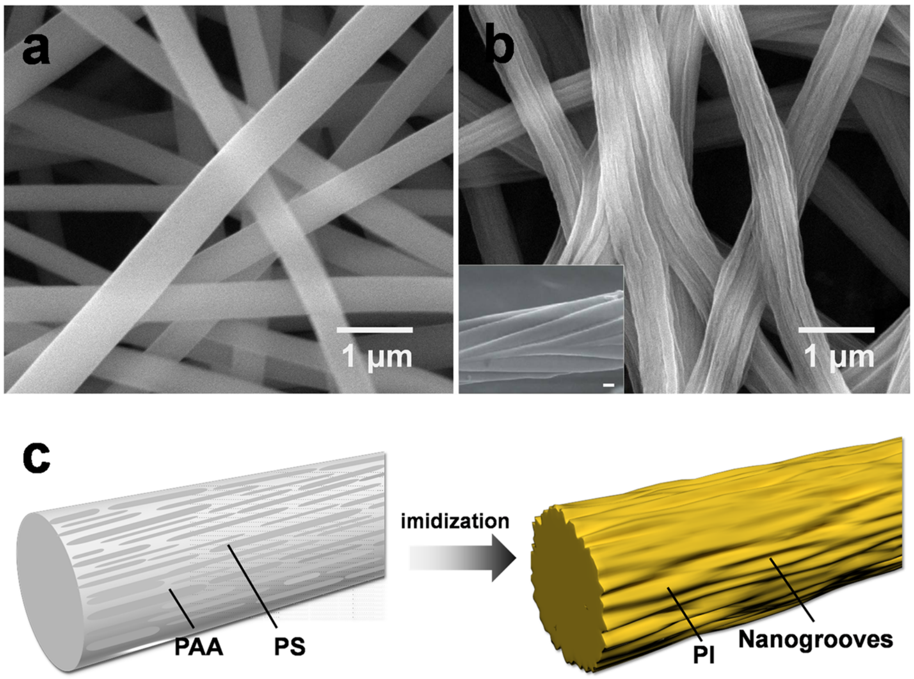
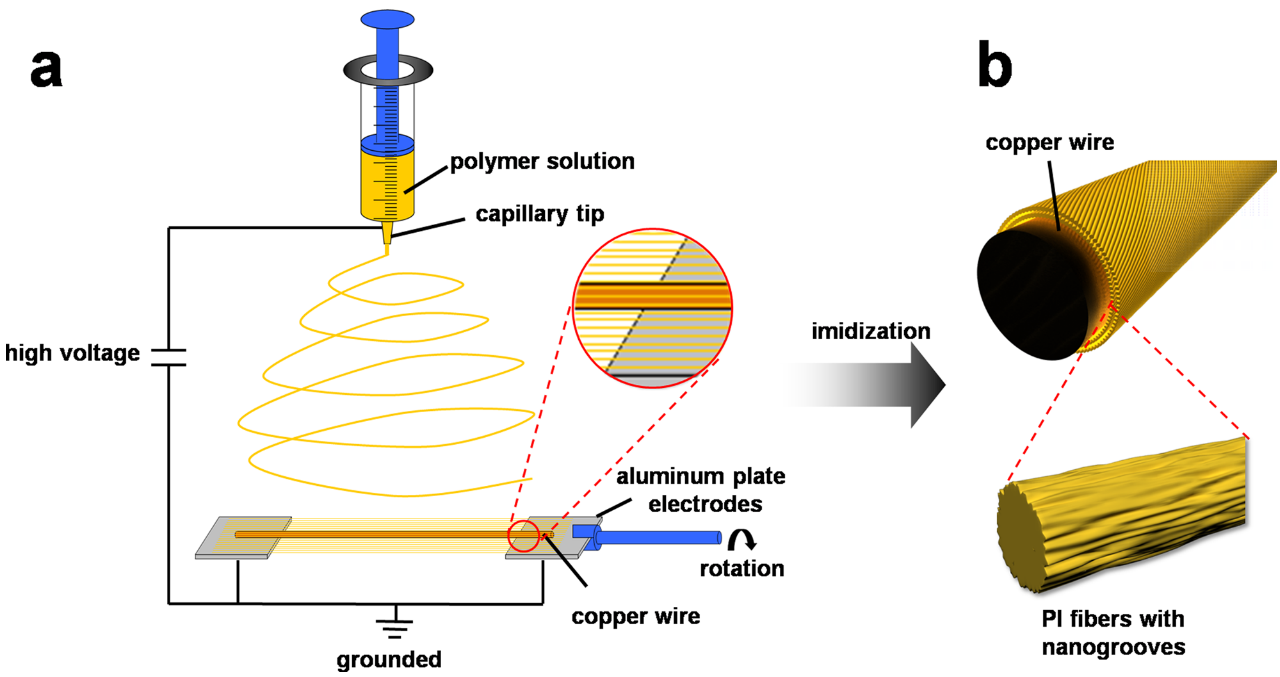


Figure 1. Formation of nanogrooved PI fibers. (a) SEM image of electrospun PAA−PS composite fibers with a smooth surface. (b) SEM image of PI fibers with nanogrooves. Inset: SEM image of a real water strider legs' fine setae. Scale bar: 200 nm.[7] (c) Schematic diagram of the formation mechanism of the nanogrooves. During the ES process, molecular chain aggregation of PS distributed the composite fibers. After the heating treatment, PS was decomposed and left behind numerous nanogrooves.

Scheme 1. Fabrication Procedure of the Artificial Water Strider Leg[a]



[a](a) Under the electric field force, the PAA−PS composite fibers spanned across the electrode gap and covered the copper wire. Then one of electrodes rotated and drove the fibers to cover the copper wire along the spiral direction. (b) After the imidization process, an artificial strider leg with nanogrooves could be obtained.

EXPERIMENTAL SECTION

Materials. 4,4′-Oxydianiline (purified by sublimation), pyromellitic dianhydride (recrystallized before use), and copper wires were purchased from LanYi Company in Beijing. Polystyrene (PS; average M_w ∼ 192000) was purchased from Sigma-Aldrich and *N*,*N*-dimethylformamide (DMF; ≥99.5%, dehydrated by molecule sieves) from Beijing Chemical Co.

Fabrication of a Model Water Strider Leg. First, a 10 wt % poly(amic acid) (PAA, the precursor of PI) solution was synthesized by a typical polymerization,[38] and a 20 wt % PS solution was prepared by dissolving PS in DMF. The two solutions were mixed in a mass ratio of 1:1 and strongly stirred at room temperature for at least 5 h to yield a homogeneous mixed solution. Second, using an improved ES system, a copper wire was put across two separate aluminum electrodes, which were both connected with the ground. The polymeric mixed solution was added in a plain plastic syringe, and a 15 kV voltage (Spellman SL50P60, USA) was applied to the nozzle. The electrospun fibers span across the gap under the action of an electric field force. Then one of the electrodes rotated along the orientation direction and drove the fibers covering the copper wire along the spiral direction. Third, the prepared artificial strider leg was heated at 120, 150, 180, 250, 300, and 350 °C to undergo an imidization process, which could turn PAA into PI.

Characterization. The morphologies were characterized by environmental scanning electron microscopy (ESEM, Quanta 250 FEG). Also, the supporting force of a single artificial strider leg against the water surface was measured by fixing it on the cantilever in a high-sensitivity balance (DCAD, Dataphysics, Germany).[24] The cantilever pushed the leg to press the water surface at a constant speed of 0.05 mm s^{-1} until it pierced it, and the force−distance cure could be recorded automatically. The water contact angles were measured on an OCA20 contact angle system (Dataphysics, Germany) at ambient temperature.

RESULTS AND DISCUSSION

In order to obtain the special nanogroove structure, we utilized the sacrificial template method and an easy decomposition template polymer, PS, to fabricate a kind of electrospun PI fiber with numerous nanogrooves on the surface (as shown in Figure 1). The mixed solution of PS and PAA was stirred to obtain a uniform dispersive mixture and electrospun into composite fibers at room temperature. During the ES process, the tangled molecular chain aggregations of PS were stretched and distributed in the composite fibers along the longitudinal direction. In the following thermal imidization, the sacrificial PS was decomposed so that numerous nanogrooves were left behind. As a result, the nanogrooved PI fibers were formed, and they presented morphologies similar to those of the setae of the water strider. A schematic diagram was presented to illustrate the forming process (as shown in Figure 1c).

Aiming to mimick the real water strider leg, we designed an ES system to fabricate an artificial strider leg. The prepared PAA−PS composite fibers span across the electrode gap, and a rotating electrode covered the fibers over the copper wire skeleton (as shown in Scheme 1). After the imidization process, an artificial strider leg with refined structures of nanogrooves was obtained. The morphology of the prepared leg was observed by ESEM. From Figure 2, it could be seen that the nanogrooved PI fibers covered the copper wire along the spiral direction uniformly and a lot of micrometer gaps existed among the fibers, which just looked like those between the setae of a real water strider. On the other hand, even though there were some differences in the angle, number, and size of setae between the artificial leg and real strider leg, the morphologies of the prepared "leg" were still similar to those of a real strider leg to a large extent. Also, it still could be used as a replica for the real water strider leg. Thus, we mimicked not only the nanogroove structure of setae from microscopic but also the water strider leg from macroscopic.

For the as-prepared artificial strider leg, a water-surface-piercing measurement was taken to test the repellent force by using a highly sensitive balance. As comparisons, other two types of artificial "legs", bare copper wire (leg 1) and "legs" with smooth electrospun PI fibers (leg 2, as shown in Figure S1 in the Supporting Information, SI), were tested under the same conditions. As shown in Figure 3a, the values of maximal dimple depth (MDD) and maximal supporting force (MSF) of the three artificial legs increased in sequence. The leg with copper wire could only generate a MDD of about 2.0 mm and a MSF of less than 130 dyn cm^{-1} (1 dyn = 10^{-5} N). When the smooth PI fibers were covered on the copper wire (leg 2), MDD and MSF were enhanced to about 3.0 mm and 174 dyn cm^{-1}, respectively. Furthermore, the introduction of nanogroove structure (leg 3) directly pushed the value of MDD to 4.32 ± 0.01 mm, which was almost equal to the 4.38 ± 0.02 mm of a real water strider leg. Also, MSF of a nanogrooved artificial leg was approximately 237 dyn cm^{-1}, which increased about 80% over the leg with copper wire and 40% over the leg with smooth PI fibers. Obviously, compared with the smooth structure of PI fibers, the introduction of nanogroove structure could make a significant contribution to the values of MDD and MSF. The possible reason could be explained as follows: The hierarchical micro/nanoscale structure could be considered as a multiphase surface, which was composed of air and solid. Also, the introduction of numerous nanogrooves would increase the roughness greatly, which could be helpful to trapping more air instead of water around the fiber surfaces. Thus, the artificial strider leg with nanogrooves possessed the best water-repellent property.

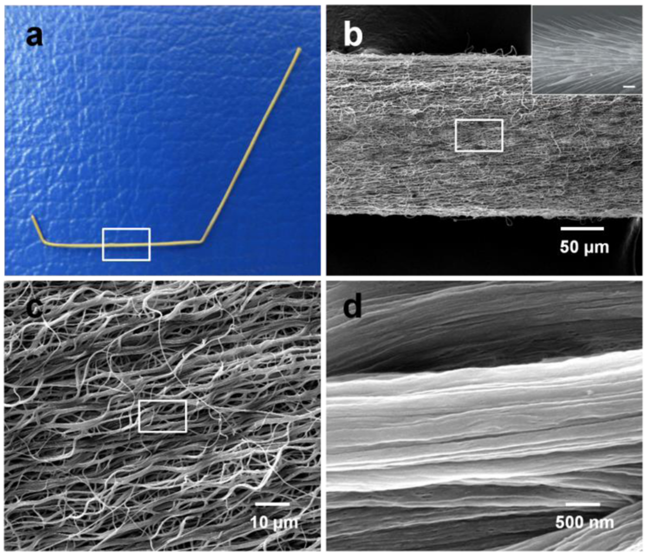


Figure 2. (a) Optical image of the artificial strider leg with nanogroove structure. (b) Enlarged SEM image of the outlined area of part a. Inset: SEM image of a real water strider leg. Scale bar: 20 μm.[7] (c) Enlarged SEM image of the outlined area of part b. (d) Enlarged SEM image of the outlined area of part c, the nanogrooved PI fibers.

To further demonstrate the excellent performance more simply and visually, we have fabricated a biomimetic model water strider with an aluminum foil body and four artificial strider legs (as shown in Figure 3b). Also, the effective rowing segment of the model strider leg was about 10 mm in length. This model strider could stand on the static water surface easily and move steadily, despite of its heavier metal body than a real insect (seen in the SI). On the other hand, when we place the model strider on a dynamic water surface, such as a boiling water surface, it also could show remarkable water-standing ability. The legs did not pierce the dimples even though the rolling water surface brought extra kinetic energy to the model strider (seen in the SI). Furthermore, to our surprise, when we put a 370 mg button (about 5.5 times the weight of the model water strider) on the back of the model strider, its legs created

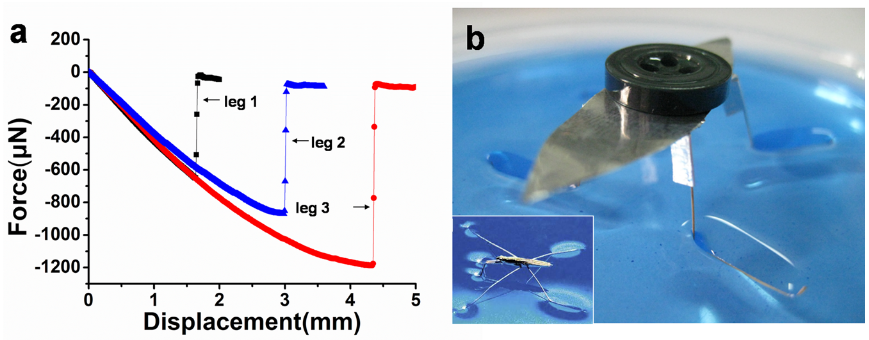


Figure 3. (a) Curve indicating the supporting force and dimple depth of "legs" with copper wire (leg 1), smooth PI fibers (leg 2), and nanogrooved PI fibers (leg 3). (b) Model water strider of around 45 mm in length and 67 mg in weight carrying a 370 mg button and still able to stand on the water surface. Inset: Photograph of a real water strider.[19]

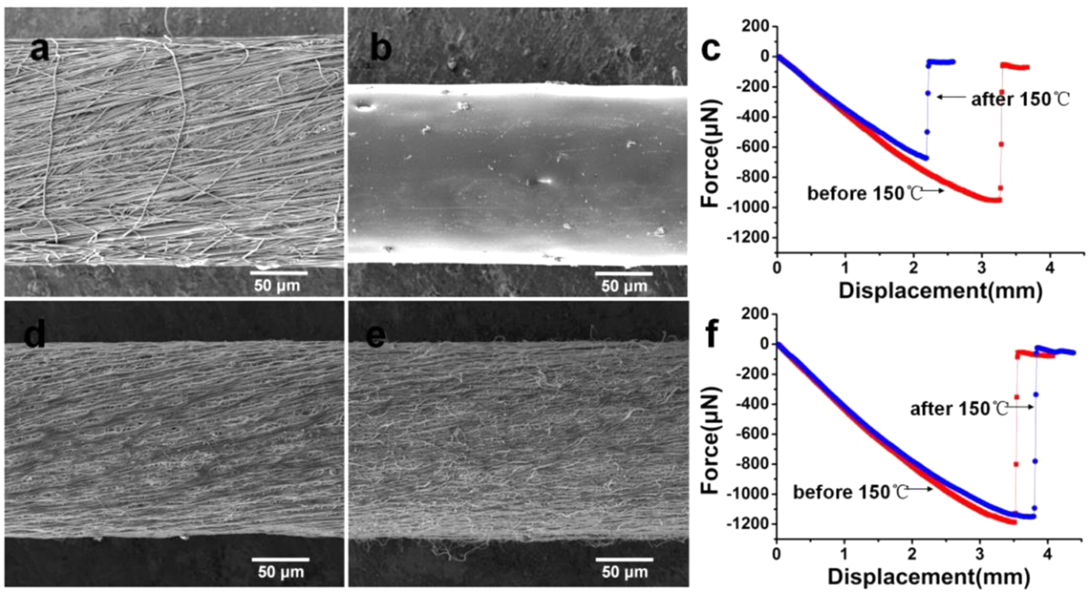


Figure 4. Comparison of the thermal stability and water-repellent performance of "legs" covered with PS fibers and nanogrooved PI fibers, respectively. After 150 °C heating, (a−c) the PS fibers melted into a film and the values of MDD and MSF fell sharply, (d−f) while the microstructure of an artificial leg with nanogroove structure had no changes and the corresponding MDD and MSF were almost at the same level.

four larger dimples, as shown in Figure 3b (seen in the SI). Also, under the action of an external force, the loaded model strider also could march steadily on the water surface. In order to test the maximal load capacity of the model water strider, we added water droplets on the back of the model strider continuously until it sank. To our surprise, 478.5 mg of water (about 7 times the weight of the model water strider) could be carried at most by this model strider. The above results demonstrated that the artificial strider leg with nanogroove structure could provide a huge supporting force for the model strider.

Because we know that PI is a type of high-performance polymer, we expected that the as-prepared artificial leg would be thermally stable and its water-repellent performance could be preserved after thermal treatment. Therefore, a heat treatment was carried out to study the thermal stability and its effect on the water-repellent property. As a comparison, another "leg" consisting of neat electrospun PS fibers was also studied. After a 150 °C treatment for 0.5 h, the PS fibers had already melted into a layer of smooth thin film, and the micro/nanostructure had been ruined completely (as can be seen in Figure 4a,b). A sharp falling of MDD and MSF also could be observed from Figure 4c. This was because T_g of PS is relatively low. The water-repellent property of an artificial leg with PS fibers could only be maintained in a narrow temperature range, which limited its application in hot conditions. On the other hand, after heating under 150 °C for 30 min, the fine hierarchical structure of the nanogrooved artificial leg was unharmed, so that the corresponding MDD and MSF were almost kept in the same level (Figure 4d,f). Actually, this nanogrooved "leg" could even tolerate higher temperature, as hot as 300 °C, and still maintain a nice water-repellent performance. So, the artificial strider leg with nanogrooves had excellent thermal stability and could be applied in harsh conditions. The foretold movie that a model strider could walk on a boiling water surface also supported our conclusion (seen in the SI).

In addition, apart from the great contribution to the water-repellent ability, we were also curious about whether the nanogroove structure had an influence on the hydrophobic property. So, two kinds of electrospun PI fibrous mats (consisted of smooth and nanogrooved structures) were prepared to compare the wettabilities. The morphologies of the samples were measured by ESEM, and the hydrophobic properties were tested by a contact-angle system. As shown in Figure S2 in the SI, the contact angles were 129.1° and 134.0°, respectively. Compared with the 67.8° of a casting PI film, the electrospun PI mats exhibited hydrophobicity. As to the nanogrooved mat, the introduction of finer nanostructures helped little in the further enhancement of its hydrophobicity. However, even so, our nanogrooved artificial strider leg could still possess excellent water-repellent performance, indicating that a superhydrophobic surface was not the sole condition to obtain high antiwater force.

■ CONCLUSIONS

A kind of artificial strider leg with refined nanogroove structure and excellent water-repellent performance has been simply and effectively designed and fabricated by ES. The prepared model water strider with the nanogrooved "leg" could carry a load that was 7 times heavier than its own weight at most. Meanwhile, even though the artificial leg with nanogrooves did not come to the superhydrophobic state, it still had a high antiwater force. This biomimetic "water strider leg" also had great thermal stability, and it could facilitate the development of water-walking devices for exploring and monitoring the harsh environment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

SEM characterization of the "leg" with smooth PI fibers and electrospun PI fibrous mats and movies of the model water strider's floating behavior on a water surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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