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REVIEW

Engineering biomimetic superhydrophobic surfaces of electrospun nanomaterials

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Summary Biomimetics provides a model for developments of functional surfaces with special wettability. Recently, manufacturing bio-inspired superhydrophobic surfaces has become an increasingly hot research topic. The electrospinning technique is a versatile and effective method for manufacturing nanomaterials with controllable compositions and structures, and therefore provides an ideal strategy for construction of superhydrophobic surfaces on a large scale. After a brief description of several superhydrophobic surfaces inspired by nature, we highlighted the recent progresses in design and fabrication of these bio-inspired superhydrophobic surfaces via electrospinning technique. The studies on the switchable wettability of nanofibrous surface brought about by external stimuli are also addressed. We conclude with a summary of current and future research efforts and opportunities in the development of electrospun nanomaterials for superhydrophobic applications.
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Introduction

The wetting behavior of a liquid on a solid surface is a very crucial aspect of surface properties, which plays important roles in industry, agriculture, and daily life [1,2]. Studies of non-wettable surfaces with a water contact angle (WCA) close to or higher than 150° and facile sliding of drops, also called superhydrophobic surfaces [3,4], have a long history back to 1907 when Ollivier noticed that contact angles of nearly 180° on the surfaces coated with soot, arsenic trioxide and lycopodium powder [5]; but until mid-1930s this

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phenomena gained substantial attention evidenced by the first outlined principles of superhydrophobicity by Wenzel [6] and Cassie [7]. Superhydrophobic surfaces have attracted rapidly growing interests in the past two decades triggered by discovery of ''lotus effect'' originated from mimicking the lotus leaves, which causes water and even oils to roll off with little or no residue left and any resting surface contamination carried away [8]. Besides the lotus leaves, nature also abounds with other mysterious biological organisms that exhibit excellent superhydrophobicity, such as silver ragwort leaves [9,10], ramee leaves [11], Chinese watermelons [11], water-strider legs [12], rice leaves [13], bamboo leaves [14], and waterfowl feathers [15]. Learning from nature gives us much inspiration to engineer desired wettability on functional surfaces through cooperating hierarchical structures and other specific components on these natural surfaces [2,16]. Since Onda's group first demonstrated artificial superhydrophobic surfaces in mid-1990s [17], various mechanisms have been proposed for the preparation of fine surface geometrical structures such as template synthesis, phase separation, electrochemical deposition, electrohydrodynamics, crystallization control, chemical vapor deposition (CVD), and self-assembly. These mechanisms have been reviewed in a number of publications [3,18]. Fundamentally, significant progress of the classical models as well as recent experimental research have revealed that the surface structure or roughness with a length on the micrometer or nanometer scale plays a key role in realization of superhydrophobic surfaces [19].

Over the past two decades, the developments of nanoscience and technology have created various nanostructures in forms such as nanoparticles, nanofibers, nanowires, nanotubes, and nanobelts [20]. As a nanofabrication technique, electrospinning has been identified as a remarkably robust and versatile method for fabricating fibers with diameters down to the nanometer length scale by applying a high voltage on a polymer solution or melt [21,22]. A variety of materials such as polymers, ceramics and even metals have been electrospun into uniform fibers with well-controlled sizes, compositions, and morphologies [23,24]. Different nanofiber assembly morphologies can be fabricated via control of the processing conditions or collector shapes to produce fibrous nonwovens with random oriented, aligned [25] as well as patterned [26] and spider-web-like nanofiber/net [27] structures (Fig. 1a—d). Through regulating the processing parameters or designing appropriate spinnerets, recent demonstrations imply that this technique can also prepare single nanofibers with bead-on-string, ribbon-like [28], helical [29], porous [30], necklace-like [31], firecracker shape [32], rice-grain shape [33], core—shell [34], multichannel tubular [35], multi-core cable-like [36], tube-in-tube [37], nanowire-in-microtube [38] and hollow [39] structures (Fig. 1e—q). It has been shown that the outstanding properties and multifunctionality of such nanofibers are highly attractive to numerous applications including biotechnology, textiles, filters, composites, sensors, and so on [23,33,40]. Additionally, this technique has become particularly powerful when combining other remarkable features, such as enormous surface-to-volume ratio and pore sizes in nano range of nanofibers, with unique chemical, physical, and mechanical functions provided by adding other components with ease and control [41]. Not surprisingly, electrospinning opens a door to tailing materials and creating various micro- or nanostructures for superhydrophobic surfaces.

This review will focus on the most recent developments of the electrospun materials for constructing bio-inspired superhydrophobic nanofibrous surfaces, which mainly include popular strategies for fabricating rough surfaces inspired from nature, how to introduce low-surface-energy coatings or surface modification treatment on these rough surfaces and then directly electrospinning the low-surface-energy materials. Then, we outline the current state-of-the-art research on the switchable wettability of surface brought about by external stimuli. Finally, we provide conclusions about this review and also provide prospects on the future of this topic.

Electrospun superhydrophobic structures inspired by nature

Nature has built a tremendous number of fascinating materials and structured surfaces with excellent surface wettability. Biomimetic investigation indicates that some natural phenomena, such as the self-cleaning effect of lotus and silver ragwort leaves [9,42], the superhydrophobic forces exerted by a water strider's leg [12], the anisotropic de-wetting behavior of rice leaves and waterfowl feathers [13,14], are all related to their unique micro- or nanostructures on surfaces [43]. On the other hand, electrospinning has become one of the most popular methods for the fabrication of micro- and nanofibrous materials with controllable compositions and structures in recent years, and therefore offers excellent prospects for construction of biomimetic superhydrophobic surfaces. In this section, we will introduce the recent progress of some electrospun superhydrophobic structures inspired by nature.

Hierarchical structures inspired by lotus leaf

In nature, many plant leaves exhibit remarkable superhydrophobic properties [2,11]. The self-cleaning lotus leaf is among the most well-known and studied examples, which exhibits a high WCA of around 161° and a small sliding angle about 2° [2,44]. Raindrops are almost spherical on lotus leaf surface and able to roll off easily, which is usually referred to as the well-documented ''lotus effect'' (Fig. 2a). In 1997, Barthlott and Neinhuis firstly revealed the superhydrophobicity of lotus leaves [45]. Investigations showed that this unique property is caused by the surface micrometer-sized papillae (Fig. 2b). However, detailed scanning electron microscopy (SEM) images of lotus leaves (Fig. 2c) indicate that the surface of the lotus leaf is textured with 3—10 μm size protrusions and valleys uniformly, which are decorated with 70—100 nm-sized particles of a hydrophobic wax-like material [11]. The cooperation of these special micro- and nanoscale hierarchical surface structures and hydrophobic wax-like material is believed to be the reason for the superhydrophobicity [46]. Inspired by lotus leaf, significant advances based on electrospinning technique now allow for the preparation of superhydrophobic surfaces. Here we present only those well-developed advances, such

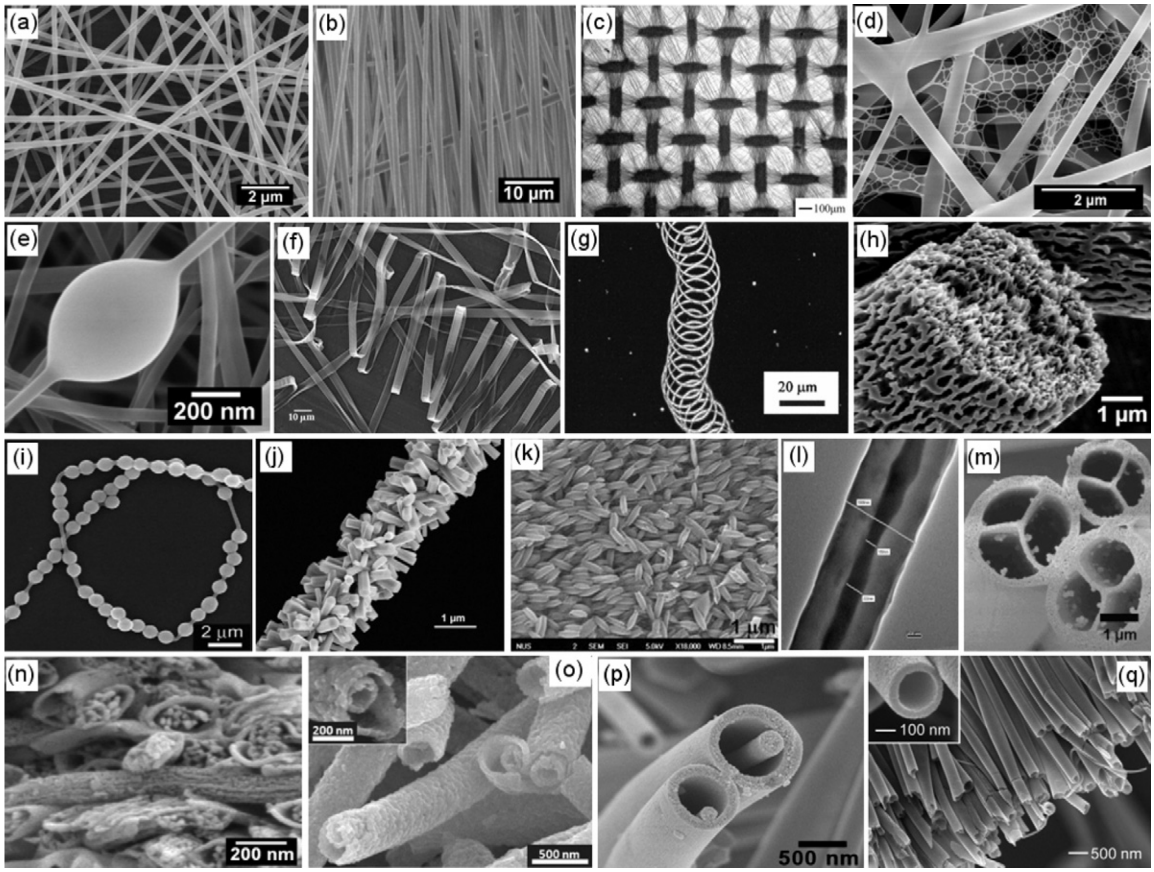

Figure 1 Various micro- and nanofibrous structures obtained by electrospinning. (a—d) Different nanofiber assembly morphologies: (a) random oriented, (b) aligned as well as (c) patterned and (d) spider-web-like nano-fiber/net structures. (e—q) Various single nanofibers with (e) bead-on-string, (f) ribbon-like, (g) helical, (h) porous [30], (i) necklace-like, (j) firecracker-shaped, (k) rice grain-shaped, (l) core—shell, (m) multichannel tubular, (n) multi-core cable-like, (o) tube-in-tube, (p) nanowire-in-microtube and (q) hollow structures.
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as one-step electrospinning, layer-by-layer (LBL) assembly, and superhydrophobic inorganic materials.

One-step electrospinning

Inspired from the fascinating hierarchical structure of lotus leaf to yield surfaces that can be cleaned by a simple rainfall, a great many artificial superhydrophobic self-cleaning surfaces have been fabricated by creating appropriate surface chemical compositions and the hierarchical surface geometrical structure [47—49]. As might be expected for rough and hydrophobic surfaces, electrospun surfaces showed excellent superhydrophobicity [50]. Microsphere/nanofiber composite films biologically inspired to imitate the self-cleaning properties of the lotus leaf were formed by carefully controlling the concentration of the polystyrene (PS) solution during electrospinning. As shown in Fig. 2d, porous microspheres contribute to the superhydrophobicity by increasing the surface roughness, while nanofibers interweave to form a stable multilayer three-dimensional (3D) network and reinforce the composite film that is surprisingly similar to a lotus leaf [47]. Besides, a polyaniline (PANI)/PS composite film with a lotus-leaf-like structure was also successfully fabricated by electrospinning method. The PANI/PS composite film exhibits stable superhydrophobicity and conductivity, even in many corrosive solutions [51]. Yoon et al. [52] reported the fabrication of a biomimically designed superhydrophobic poly(ε-caprolactone) (PCL) surface, which was obtained using a modified electrostatic process. The fabricated surface exhibits a micrometer-sized pyramid structure consisting of accumulated droplets and nanofibers (Fig. 2e). Nanofibers prepared by electrospinning usually exhibit

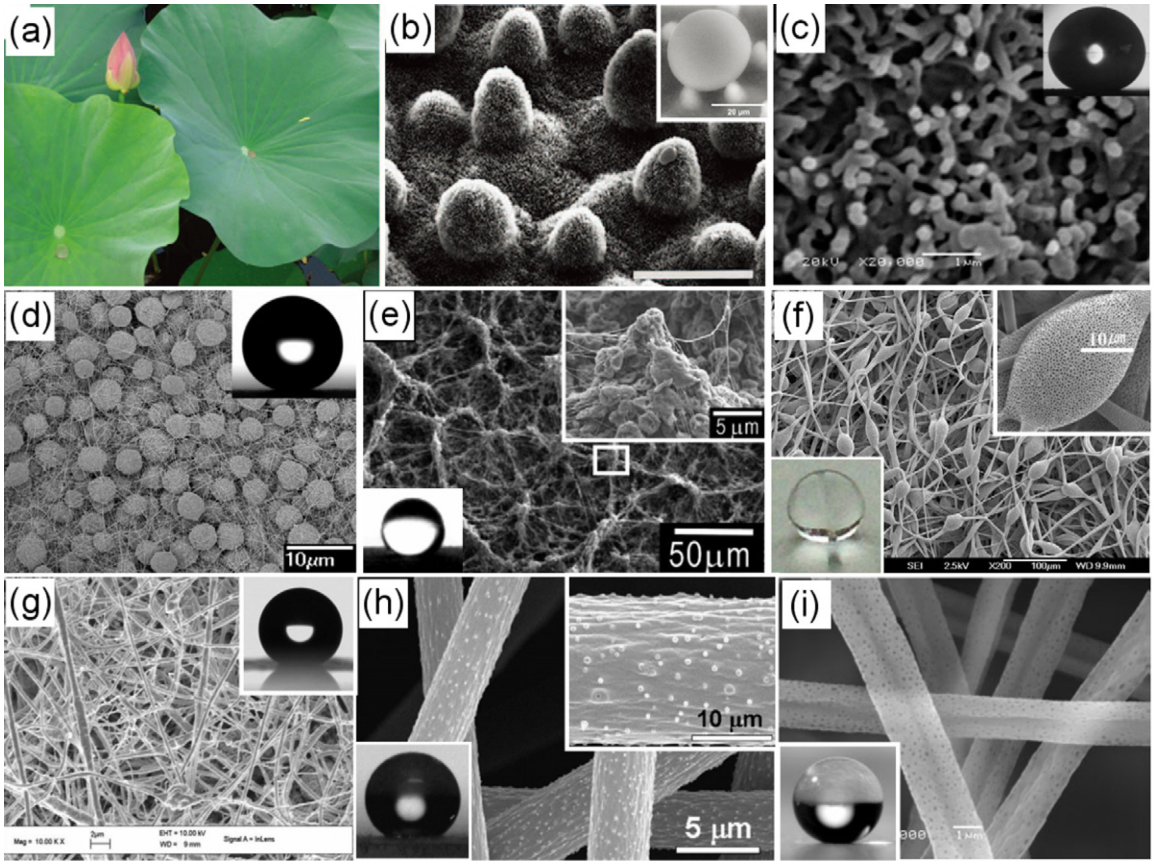

Figure 2 Superhydrophobic surfaces inspired by lotus leaf. (a) Lotus leaves show self-cleaning properties, note that dust is accumulated in the water droplet at the center of the leaves. SEM images of surface structures on the lotus leaf with low (b) and (c) high magnifications. The scale bar in (b) represents 20 μm. (d—i) SEM images of various superhydrophobic structures prepared via electrostatic process (electrospraying, electrospinning): (d) PS films with special microsphere/nanofiber composite structures, (e) surface consisting of accumulated PCL droplets and fibers sprayed during 2 h, (f) PHBV fibrous surface with bead-on-string structure, (g) PS—IL composite nanofiber, (h) electrospun PS fibers from 35 wt% solution in DMF and (i) PPFEMA-coated PMMA porous fibers.
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beaded fiber structures (bead-on-string structure), which are greatly influenced by the solution properties. Generally, beaded fibers have been considered as undesirable or defective products [53]. However, extensive studies have demonstrated that beaded fibers have increased hydrophobic property [53—55]. Especially, porous beaded fibers exhibit strong superhydrophobic properties [53]. For example, a poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) fibrous surface with various bead-on-string structures exhibited a further enhanced WCA (141°) than that (86°) of flat film (Fig. 2f).

Apart from these so-called defective structures, processing a secondary topography onto the rough surface of electrospun fibers to obtain a hierarchical structure is an alternative method to imitate the lotus leaf. PS—ionic liquid (IL) composite nanofibrous membranes with micro- and nanoscale hierarchical structures were successfully produced by an electrospinning method (Fig. 2g). The electrospun PS—IL composite fibrous membranes displayed both superhydrophobicity and conductivity, which may be ascribed to the hierarchical structure of the membranes and the intrinsic hydrophobicity and conductivity of the IL [56]. Kang et al. [57] recently reported a significant increase in superhydrophobicity for PS fibers containing numerous nanometer-scale protuberances which is similar to natural lotus leaves (Fig. 2h). The WCA was remarkably increased to $154.2 \pm 0.7°$, outperforming smooth PS films that showed a lower WCA (<100°). Ma et al. [49] have also shown higher contact angles and lower hysteresis using fibers 'decorated' with nanometer-sized pores (Fig. 2i). Electrospinning provides the potential to one-step fabricate superhydrophobic surfaces, however, developing other facile methods (e.g. LBL assembly) to prepare hierarchical structures inspired from lotus leaf is still a challenge.

LBL assembly

The LBL assembly process involves the sequential adsorption of oppositely charged materials to construct conformal

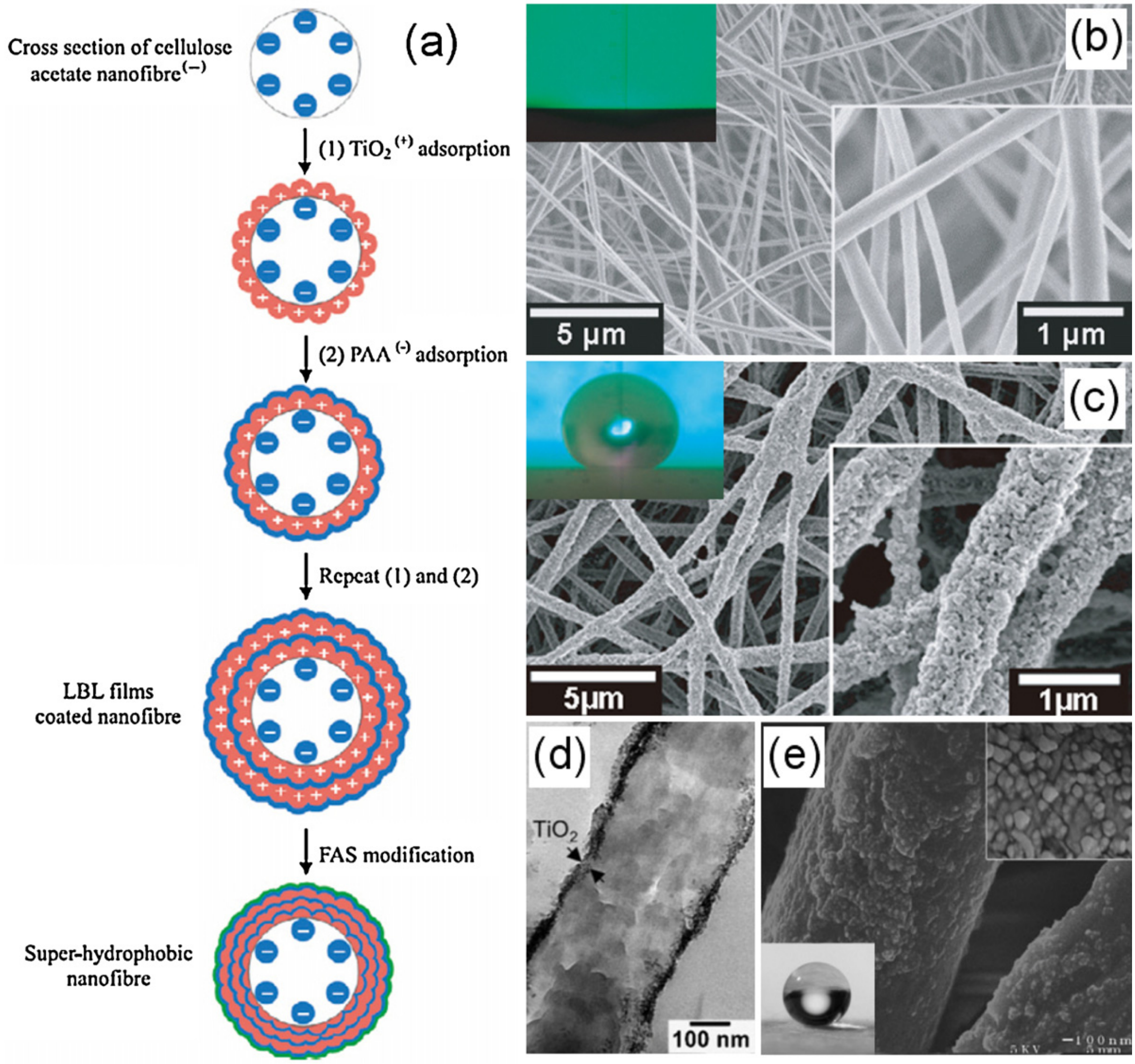

Figure 3 (a) Schematic diagram illustrating the preparation of super-hydrophobic surfaces via LBL coating and FAS surface modification. SEM images of (b) cellulose acetate fibrous membranes, (c) cellulose acetate fibrous membranes deposited with 10 bilayers of TiO_2/PAA. (d) TEM image of TiO_2-coated PSEI fibers in longitudinal view. (e) SEM image of electrospun nylon fibers after silica nanoparticle and trichlorosilane treatment. Upper inset is the AFM phase image.
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ultrathin film coatings with controlled film thickness and chemical properties (Fig. 3a) [58]. It is therefore of interest from both scientific and technological standpoint to determine if superhydrophobic surfaces can be created from multilayer films. Such conformable superhydrophobic surfaces would have applications as antifouling, self-cleaning and water resistant coatings and coatings for microfluidic channels and biosensors [59]. Shiratori et al. [60] firstly demonstrated that the superhydrophobic behavior of the lotus leaf structure can be mimicked by creating a rough surface texture through heating polyelectrolyte multilayer films containing silica nanoparticles. Since then, LBL assembly has been widely used to construct superhydrophobic coatings on thin films and silicon wafers [59,61]. Ma et al. [49] firstly introduced the LBL technique into the electrospun fibers to construct superhydrophobic surfaces. Electrospun nylon membranes with a uniform fiber diameter of about 1.7 μm were coated with positively charged poly(allylamine hydrochloride) and negatively charged 50 nm silica nanoparticles by using the LBL self-assembly technique, followed by reaction of the surface-exposed silica with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane ($(CF_3)(CF_2)_5(CH_2)_2SiCl_3$). The average contact angle for the treated fiber mat was 168°, which could be attributed to the high density of nanoparticles decorated on the surface of treated fibers (Fig. 3e). This contact angle did not change as the droplet evaporated, indicating a stable superhydrophobicity with almost zero contact-angle hysteresis [49]. Ogawa et al. [58] demonstrated that the hierarchically roughened membranes could be prepared by alternating depositions of 7 nm diameter TiO_2 nanoparticles and poly(acrylic acid) on cellulose acetate fibers (Fig. 3b). A membrane with 10 bilayers of LBL coating (Fig. 3c) showed the highest WCA of 162° and lowest water-roll angle of 2° after surface modification with a fluoroalkylsilane (FAS). In contrast, fibrous membranes consisting of smooth fibers without FAS coatings presented superhydrophilicity (Fig. 3b, inset). The enhancement of hydrophobicity introduced by the LBL coating was attributed to the increased roughness of individual fibers and improved adsorption of fluoro groups during FAS surface modification. Lee et al. [62] reported that the combination of TiO_2 nanoparticles and nanoscale electrospun poly(dimethylsiloxane-b-etherimide) (PSEI) fibers via LBL self-assembly process can lead to a remarkable increase in the number of reactive sites, with a corresponding improvement in photocatalytic activity. Transmission electron microscopy (TEM) image in Fig. 3d confirms the presence of TiO_2 nanoparticles, seen in dark contrast to the polymer fibers. The LBL process has been emerged as a well-known technique to fabricate conformal thin-film coatings with molecular-level and thus paved the way to create transparent superhydrophobic coatings [59].

Superhydrophobic inorganic materials

Inspired by nature, considerable efforts have been made to develop polymer-based superhydrophobic materials by creating nanometer-scale features on micrometer-scale-roughened surfaces. On the other hand, inorganic materials are potentially important for those applications in many areas that include electronics, photonics, mechanics, and sensing [63]. Modifying the surface wettability of inorganic materials is also important in many situations [64]. Over the years, considerable efforts have been extended to fabricate superhydrophobic surfaces based on inorganic fibers, including SiO_2 [54,65,66], ZnO [64], TiO_2 [67], Fe_3O_4-filled carbon nanofibers [68], etc. However, it is noteworthy that most electrospun inorganic fibers usually did not exhibit superhydrophobic properties, unless they were hydrophobically modified with fluoridebearing agents such as (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trichlorosilane (FDTS) [66], FAS [14,21,22], and 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (PFOTS) [24,25]. As shown in Fig. 4a, the basic concept of fabricating inorganic fibers was to confine colloidal particles inside electrospun nanofibers and assemble the particles during fiber thinning. Through the surface modification of the electrospun nanofibers with fluorinated silane coupling agents, superhydrophobic surfaces with low sliding angles could be prepared [66]. Recently, our group has also demonstrated the fabrication of flexible, high-heat-resistant, and amphiphobic silica membranes by surface modification of bead-on-string structured nanofibrous silica membranes (Fig. 4b and c) [54]. In contrast with common sol—gel electrospinning method to obtain inorganic fibers, nanoporous silica nanofibers assembled by silica nanoparticles were fabricated by dispersing colloidal silica particles into electrospinning polymer solutions, followed by selective removal of the polymer component. Additionally, the porous structures of fibrous silica membranes were proved to be effective to obtain superhydrophobic surfaces after the FAS monolayer modification (Fig. 4d) [65]. Nanoporous ZnO nanofibers have also been reported for use as superhydrophobic surfaces (WCA of 165°) after the surface modification with FAS (Fig. 4e) [64]. Another recent report in this area makes use of the hierarchical structured TiO_2 membranes, giving WCAs of 151° (Fig. 4f) and as high as 155° after hydrothermal treatment (Fig. 10h) [67]. Multifunctional carbon nanofibers with conductive, magnetic and superhydrophobic properties were prepared by electrospinning and low-temperature carbonization. It is worthwhile to point out that the technique utilized herein could give rise to superhydrophobic surfaces (WCA of $156.5 \pm 2.68°$, Fig. 4g) [68]. Ceramic-based superhydrophobic surfaces are potentially important for those applications where requirements such as mechanical strength, stiffness, and resistance to corrosion prevent the use of other materials. Sarkar et al. [69] have demonstrated a simple polymer-derived ceramics technique for the fabrication of superhydrophobic mats by electrospinning preceramic polyaluminasilazane followed by pyrolysis and the deposition of perfluorosilane (Fig. 4h). These superhydrophobic mats possess good chemical and thermal stability. While much progress has been made in the fabrication of superhydrophobic inorganic materials, there remain several critical issues that need to be addressed before the practical application of electrospun inorganic fibers is possible. For instance, although the fabrication of flexible inorganic superhydrophobic surfaces has been realized, thorough understanding of the mechanisms of flexibility remains a very important and challenging issue.

Hierarchical structures inspired by silver ragwort leaf

Besides the lotus leaf, some other plant leaves or epidermis such as silver ragwort (*Senecio cineraria*) leaf, ramee leaf, and Chinese watermelon use a fibrous surface structure to achieve this water repellency and self-cleaning property [11]. For example, the silver ragwort presented in Fig. 5a is one species that has superhydrophobic leaves with WCA about 147° [9]. By examining the leaf with a SEM (Fig. 5b and c), it can be observed that the leaf is densely covered by many curved fibers with diameters around 6 μm. These fibers are trichomes with unicellular or multicellular structures arising from the epidermal tissues. Moreover, the secondary structures, numerous grooves with diameters around 200 nm, are found along the fiber axis [10]. The surface of a silver ragwort leaf shows a hierarchical micro- and nanostructure which is essential for achieving a high hydrophobicity. Inspired by the silver ragwort leaf, considerable endeavor has been engaged in fabricating superhydrophobic surface through electrospinning technique [9,10,70]. Gu et al. [10] fabricated an artificial surface with superhydrophobicity and light-shielding simultaneously by simply transforming PS to the trichome-like structure. The obtained trichome-like electrospun fibers under a voltage of 20 kV using a solution containing 23% PS exhibited a high WCA as 156°. In order to mimic the hierarchical structure of silver ragwort leaf and thus achieve a higher WCA, the electrospun PS microfibers with tunable rough surface structures were prepared by electrospinning concentrated PS solutions and carefully adjusting the solvent compositions [9]. The combination of the well-developed nanotexture porous structures (Fig. 5d) inherent in electrospun microfibrous PS mats and the low surface free

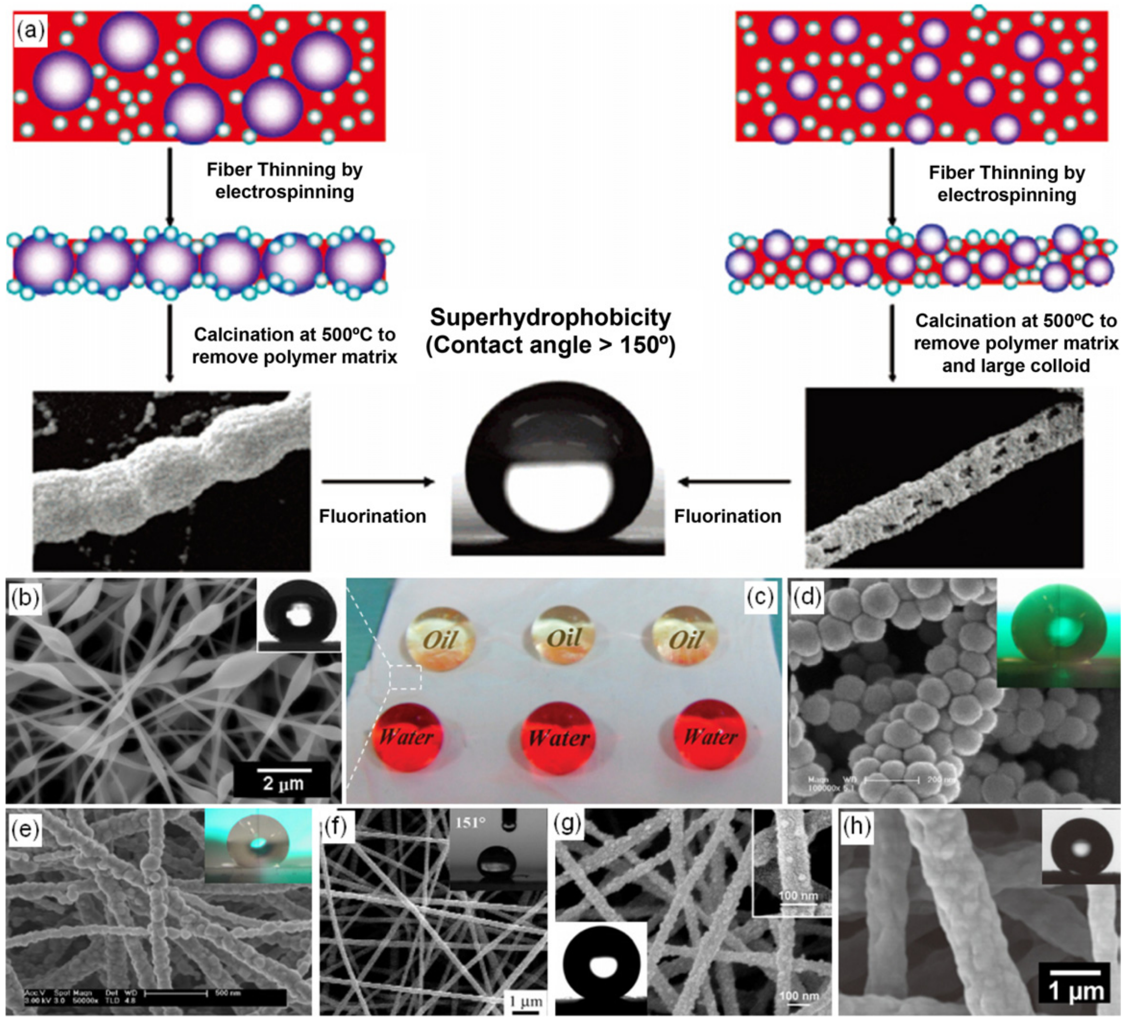

Figure 4 (a) Schematic procedures for multiple-scale inorganic fibrous structures from electrospinning. (c) Several water and dodecane droplets placed on the SiO_2 membranes (b) showing superhydrophobicity and oleophobicity. SEM images of various inorganic fibrous membranes: (d) SiO_2, (e) ZnO, (f) TiO_2 membranes, (g) Fe_3O_4-filled carbon nanofibers with 40 wt% $FeAc_2$, and (h) ceramic fibers.

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energy of PS yielded a stable superhydrophobicity with WCA as high as 159.5° for a 12 mg water droplet, exceeding that (147°) of the silver ragwort leaf. Moreover, the hydrophobicity of the porous PS mat surface was enhanced by increasing the surface roughness of the microfibers.

Mechanical robustness is of prime importance in many applications of superhydrophobic surfaces [71]. Development of durable non-wetting surfaces is hampered by the fragility of the microscopic roughness features that are necessary for superhydrophobicity. Despite the importance of mechanical durability in practical applications, this aspect has received relatively little attention until very recently, particularly for electrospun nanomaterials based superhydrophobic surfaces [70,72,73]. Recently, a large-scale silver ragwort leaf inspired superhydrophobic fibrous surface with an enhanced mechanical property by blending PS and polyamide 6 (PA6) fibers was fabricated via a four-jet electrospinning technique (Fig. 5e) [70]. The mechanical properties of PS membranes were significantly enhanced with adding the component of PA6 nanofibers in fibrous PS membranes and regulated by tuning the number ratios of jets of PS/PA6 in the four-jet electrospinning process. The fibrous membranes formed with the number ratios of jets of 2/2 (PS/PA6) showed a WCA of 150° (Fig. 5f) with a three times increased tensile strength compared with that of the pure fibrous PS mats [70]. While the fragility of superhydrophobic surfaces currently limits their applicability, development of mechanically durable surfaces will enable a wide range of new applications in the future [71].

Coaxial electrospinning expands the versatility of electrospinning by enabling the formation of core—sheath-structured micro/nanofibers. Recent reports have also

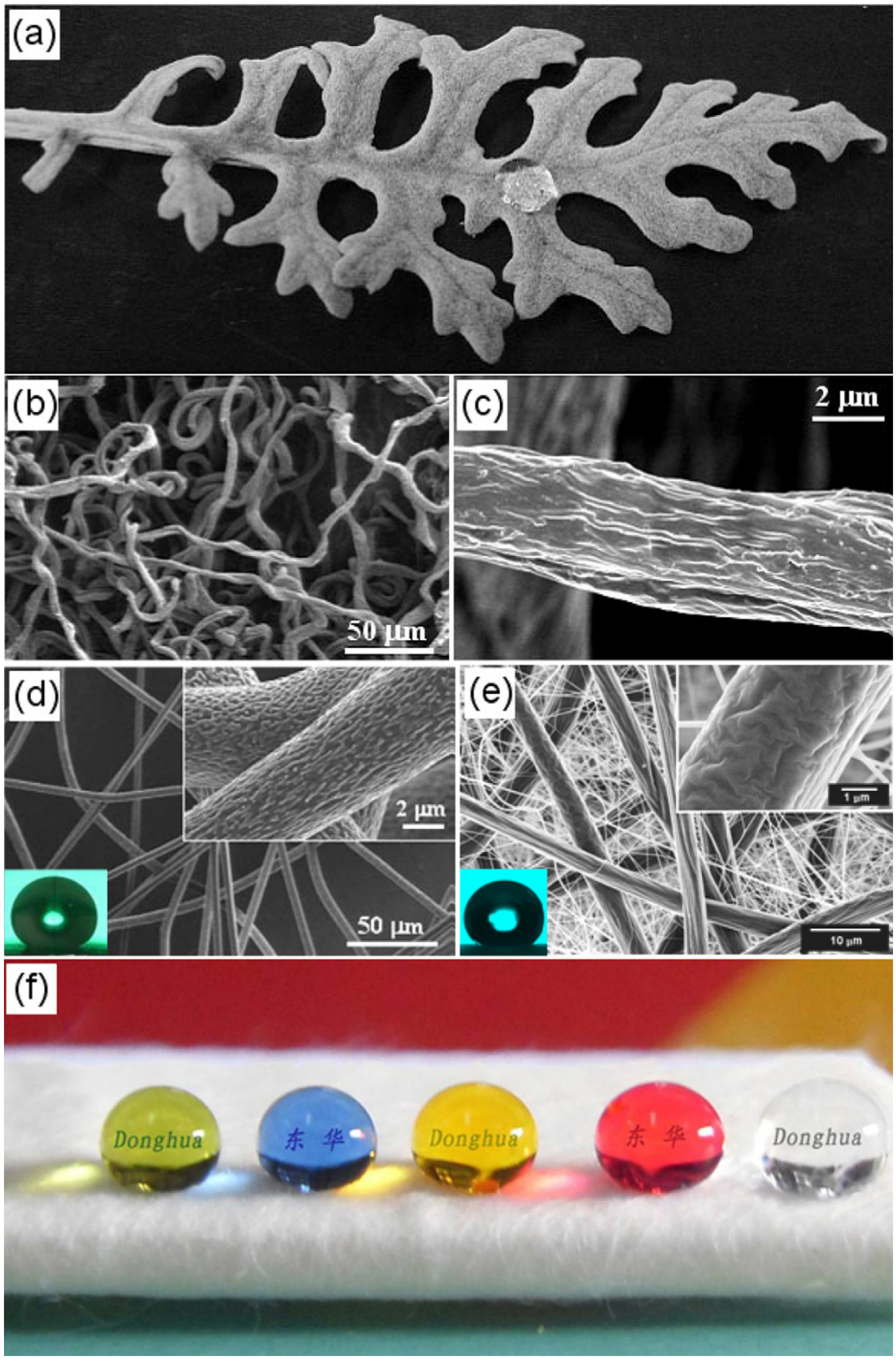

Figure 5 (a) Photograph of a water droplet on a silver ragwort leaf. (b and c) SEM images of the leaf at different magnifications. (d) SEM image of the electrospun PS fibers formed from weight ratio (1/3) of THF/DMF in solvents. (e) SEM images of fibrous mats formed with number ratio (2/2) of jets of PS/PA6. (f) Several water droplets placed on the composite PS/PA6 fibrous membranes. (d) Reprinted with permission from [9]. ©2006 IOP Publishing Ltd. (f) Reprinted with permission from [70]. ©2009 American Chemical Society.

demonstrated that the coaxial electrospinning could fabricate biomimetic superhydrophobic surface [74,75]. Han et al. [74] first demonstrated superhydrophobic PCL/Teflon amorphous fluoropolymer (AF) fibrous membranes could be produced by coaxial electrospinning (Fig. 6a—c). It is clear that the coaxial fiber membrane surface structure, which combines macroroughness (spacing between fibers) with microroughness (striation of individual fibers) (Fig. 6e and f), is similar to that of silver ragwort leaf. The electrospinnable core polymer that provides surface roughness is conformally coated with nonelectrospinnable Teflon AF fluoropolymer that provides low surface energy. The as-prepared coaxial fiber membrane showed not only good superhydrophobic properties (Fig. 6d) but also strong oleophobic properties for

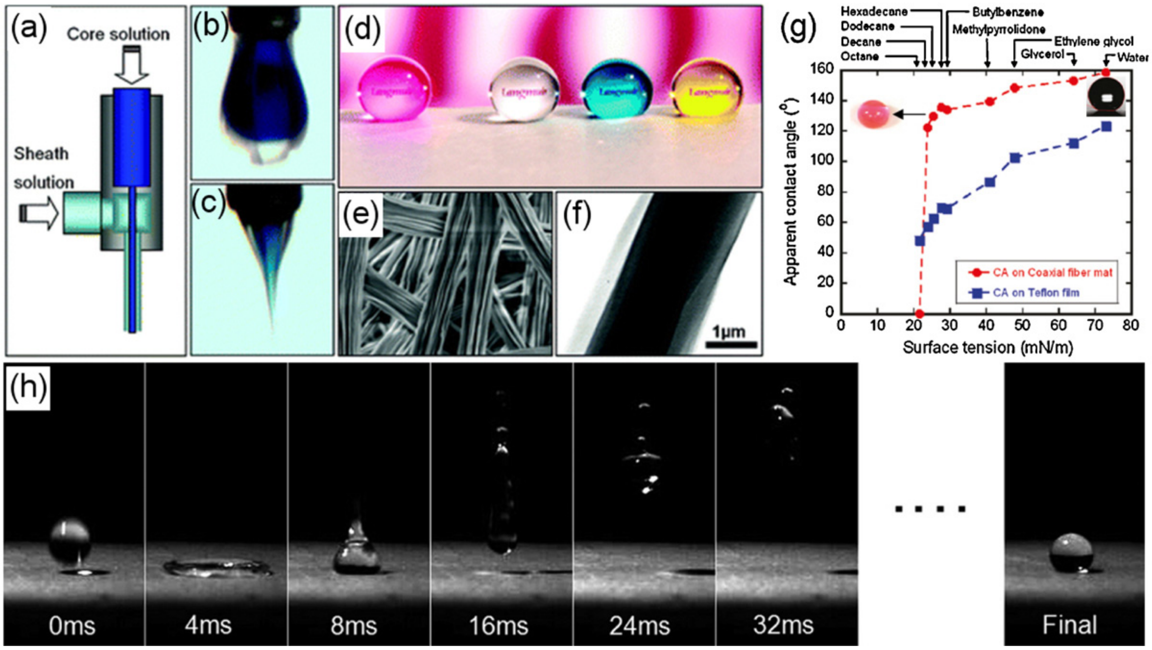

Figure 6 Coaxial electrospinning for preparing superhydrophobic and oleophobic fibers. (a) Diagram of the coaxial nozzle. (b) Core—sheath droplet without bias. (c) Taylor cone and coaxial jet formation at 12.5 kV. (d) Several water droplets placed on the composite PCL/Teflon fibrous membranes. SEM (e) and TEM (f) images of PCL/Teflon fiber. (g) Contact angles of various solvents including water and oils on Teflon films and on PCL/Teflon coaxial fiber membranes. (h) Time sequence of water droplet impact on coaxial fibrous membranes.
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all of the oils evaluated (except for octane) (Fig. 6g), which is attractive for applications in corrosive environments. Additionally, the coaxial fiber membranes show excellent water-bouncing behavior at the falling speed of 1.44 m/s with 10 μL volume (Fig. 6h). Recently, Muthiah et al. [75] reported coaxially electrospun Teflon AF-poly(vinylidene fluoride) (PVdF) and PVdF-Teflon AF core—sheath fiber mats with high surface hydrophobicity. These resultant membranes may be used in Li-air batteries as a potential membrane separator at the cathode side to prevent the entry of any large amount of water into the battery and avoid any hazardous reaction that might happen between metallic Li and water. The fact that a normally nonelectrospinnable material such as Teflon AF has been successfully electrospun when combined with an electrospinnable core material indicates the potential of coaxial electrospinning to provide a new degree of freedom in terms of material combinations for many applications [74].

Up to now, most biomimetic superhydrophobic surfaces are just limited to mimic one natural material, but there still remain many challenges in developing dual- or multi-biomimetic superhydrophobic surfaces. More recently, our group has demonstrated the fabrication of dual-biomimetic superhydrophobic fibrous mats via electrospinning PS solution in the presence of silica nanoparticles (Fig. 7) [42]. The resultant electrospun fiber surfaces exhibited a fascinating structure with the combination of nano-protrusions and numerous grooves due to the rapid phase separation in electrospinning, which imitated the structures of lotus leaf and silver ragwort leaf (Fig. 7b). Future research will undoubtedly see the investigation of natural materials and exploration of new functions. Increasing attention will be paid to the development of multifunctional structures [76].

Hierarchical structures inspired by water strider legs

Water striders (Fig. 8a) are a type of insect with the remarkable ability to stand effortlessly and walk quickly on water surfaces [77]. Jiang et al. [12] reported that the supporting legs of water strider are superhydrophobic, as the result of the combination of the uniquely hierarchical surface structure of needle-shaped micro-setae with elaborate nano-grooves and the covered hydrophobic wax layer (Fig. 8b). Further investigation of the water repellency mechanism of water strider legs based on the topography of the maximal dimple (Fig. 8c) indicated that the maximal supporting force of a single leg against water surprisingly reached up to 152 dynes, about 15 times the total body weight of this insect [78]. This striking repellent force is attributed to the superhydrophobicity on the legs, which is verified by a static WCA of about 167.6 ± 4.4° [44]. Learning from nature is an important source of new techniques and advanced materials [2]. Inspired by the hierarchical surface structure of water strider legs, Wu et al. [14] fabricated an artificial water strider utilizing electrospun nanofiber-wrapped silver wires. Affected by the repulsion force of the charges, the fibers had not aggregated and formed a porous web around the silver wire core (Fig. 8e). When floating on the water, the available air around the microstructure is trapped in spaces in the porous fibers to form a cushion

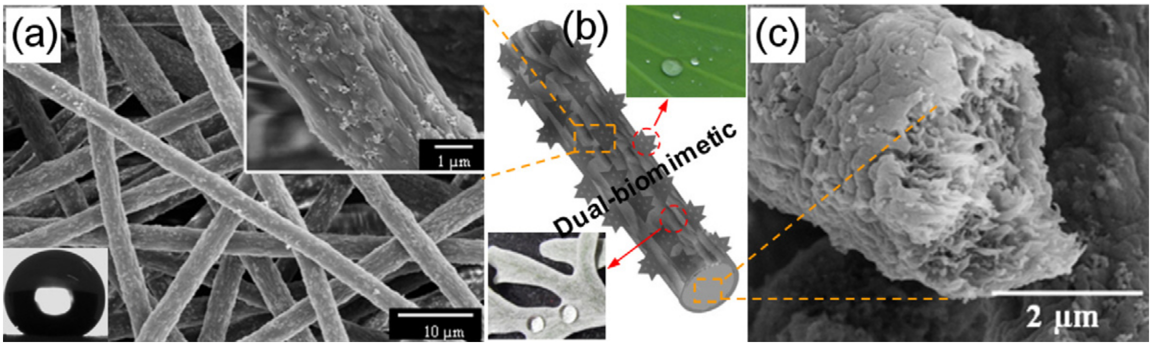

Figure 7 Dual-biomimetic superhydrophobic PS fibers biomimicked from a combination of the lotus leaf and ragwort leaf. External-sectional (a) and cross-sectional (c) SEM images of PS fibers containing 14.3 wt% silica nanoparticles formed from DMF. (b) Schematic diagram of the biomimetic superhydrophobic surfaces. Upper inset is the view of a water droplet on a lotus leaf and lower inset notes the water droplet on a silver ragwort leaf [42].
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at the leg—water interface and therefore prevents the legs from becoming wet (Fig. 8d). Moreover, the maximal supporting force of man-made leg coated with the superhydrophobic films increases at least 2.4 times compared with the bare hydrophobic copper leg (Fig. 8f) [79]. Mimicking water striders opens a facile method to develop microrobots to stand and maneuver on water [79]; an immediate work along this line would be further design of different biomimetic structures and investigation of the quantitative relationship among the maximal supporting force, the dimple depth, and the micro- and nanofibrous structures.

Anisotropic structures inspired by plants leaves and goose feathers

Biomimetic anisotropic surfaces also have attracted a lot of attention due to their important applications in microfluidic devices, evaporation-driven nanopatterns, and easy-clean coatings [10,43]. Many strategies such as interference lithography [80], photolithography [81], surface wrinkling [82], and electrospinning [14] have been developed to realize anisotropic wetting on groove microstructures. In this section, we will focus on the anisotropic wetting surfaces

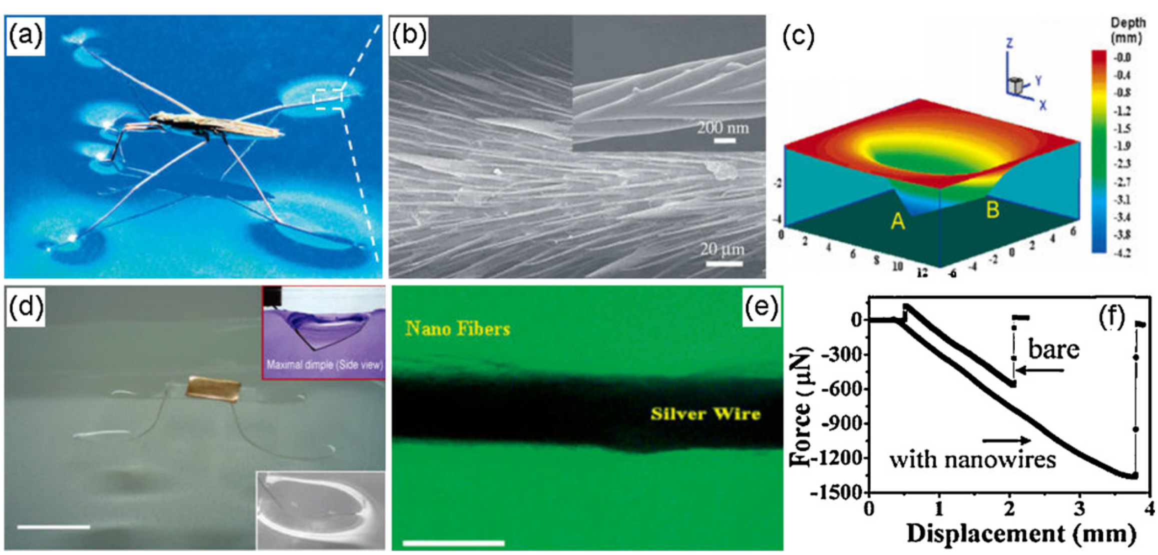

Figure 8 The superhydrophobic water strider legs. (a) Photograph of a water strider standing on the water surface. (b) SEM image of the leg with oriented spindly setae and the nanogrooves on a single seta (inset in (b)). (d) A model man-made water strider standing on the water surface. A copper strip with a mass of 0.5 g was carried. Upper inset is the side view of the strider leg walking across the water surface. Lower inset notes the deformation of the surface around the legs. Scale bar: 1 cm. (e) Optical microscopy image of one leg of the miniature water strider showing porous nanofibers coated on a silver wire. Scale bar is 200 mm. (c) 3D topography of the dimple treaded by a hind leg [78]. (f) Comparison for the supporting force of the bare hydrophobic copper leg and the superhydrophobic copper leg.
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inspired by nature and some artificial anisotropic surfaces prepared by electrospinning.

The best-known example is the natural rice leaves, which possess a hierarchical structure similar to the lotus leaves, exhibiting superhydrophobicity with a WCA of about $157 \pm 2°$ (Fig. 9a) [11]. However, further investigation of the fine structure of rice leaves reveals that the papillae are arranged in quasi-one-dimensional order parallel to the leaf edge (Fig. 9b) of the direction of arrow in Fig. 9a [11]. Consequently, the surfaces of rice leaves show anisotropic wettability and the water droplet can roll off freely along the direction parallel to the rice leaf edge but moves much harder along the perpendicular one. The sliding angles of these two directions are $\sim 3-5°$ and $\sim 9-15°$, respectively [3,11]. For the rice leaf, it is greatly influenced by the anisotropic arrangement of the papillae, while it is the same in all directions on the lotus leaf due to the homogeneous distribution of papillae. To mimic the rice leaves, anisotropic surfaces can be made by simply aligning electrospun fibers. Such surfaces can, in principle, exhibit anisotropic wetting behavior. By careful design of the fiber collector, it is possible to coat nanofibers onto conductive objects of any reasonable size or shape and make their surfaces extremely hydrophobic. For example, Ma et al. [19] fabricated aligned

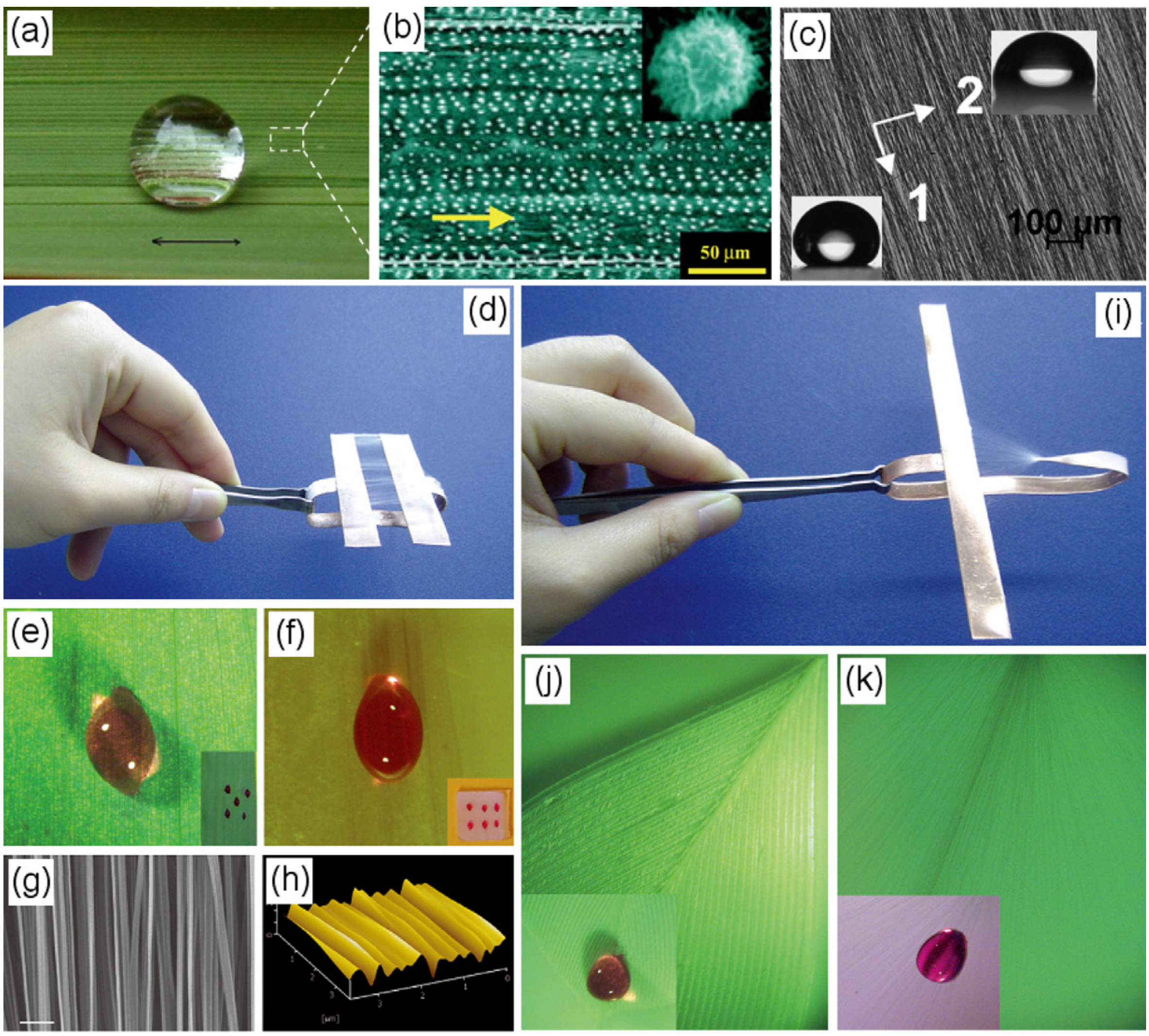

Figure 9 Anisotropic surface based on electrospun fibers. (a) Optical photo of a water droplet floating on a rice leaf. (b) SEM image of rice leaf. (c) Optical micrograph of a glass slide covered by a low density of aligned PAN electrospun fibers. Insets shows the photos of the droplet on the surface coated with PPFEMA taken from directions 1 and 2. (d) A digital photograph of the aligned fibers collected between two parallel electrodes. (e and f) A water droplet set on the surface of (e) a bamboo leaf and (f) a silicon wafer coated by aligned electrospun PVB nanofibers. (g) SEM image of aligned PVB nanofibers, scale bar is 1 mm. (h) AFM image of the fiber array. (i) Digital photograph of fan-shaped radiating nanofiber pattern collected by a spiculate copper needle perpendicular to a rectilinear copper strip. (j and k) A water droplet set on the surface of (j) goose feather and (k) fan-shaped radiating nanofiber pattern.

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electrospun polyacrylonitrile (PAN) fibers with parallel electrodes as the collecting substrate. The aligned fibers were then transferred to a glass slide and coated with polymerized perfluoroalkyl ethyl methacrylate (PPFEMA) using CVD. The resultant membranes exhibited superhydrophobic behavior with a WCA of 153° and a threshold sliding angle of 8° in the direction parallel to fiber axis, and a non-superhydrophobic behavior (WCA of 119°) in the perpendicular direction (Fig. 9c). The anisotropy is probably attributed to differences in contact lines formed parallel and perpendicular to the fibers. The sliding angle also varies with direction, due to the fact that the droplet has to overcome an energy barrier to spread from fiber to fiber in the direction perpendicular to the fibers, while there is no such barrier to spreading along the fibers. Mizukoshi et al. [83] have also demonstrated that the patterned surface composed of aligned electrospun fibers showed anisotropy for both the wetting and sliding behaviors.

Anisotropic surface patterning is not limited to natural rice leaves. Some other plant leaves and waterfowl feathers also have special surfaces with anisotropic wetting properties [14,16]. For example, water droplets on a bamboo leaf and a goose feather are not spherical but elliptical and streamlined, respectively (Fig. 9e and j) [14]. These anisotropic wetting phenomena are attributed to the alignment of the leaf and feather veins. Mimicking the topography of the bamboo leaf surface, Wu et al. [14] fabricated aligned poly(vinyl butyral) (PVB) fibrous membranes by utilizing two parallel copper strips as fiber collectors (Fig. 9d). As observed from the SEM and atomic force microscopy (AFM) images (Fig. 9g and h), the fibers with diameters of about 100 nm are well arranged and form a uniaxially aligned dense array. Fig. 9f displays the microscopy image of a water drop on the patterned fiber, showing the elongation of the droplet along the fibers as well as anisotropic wetting characteristics. Following this approach, they also produced goose feather-like biomimetic fan-shaped radiating nanofiber pattern by collecting fibers between the metal needle and the straight strip (Fig. 9i–k), which could further lead to a similar wetting anisotropy. Taking advantage of this easy and fast fabrication method, patterned electrospun nanofibers provide a new platform to realize functional surfaces with desired wetting properties on a large scale [14].

Constructing superhydrophobic surfaces by surface modification

Studies on the biomimetic superhydrophobic surfaces indicate the importance of the surface morphologies for constructing the surfaces with hierarchical or anisotropic structure. The above-mentioned examples have also witnessed that some electrospun hierarchical or anisotropic surfaces cannot possess superhydrophobicity unless they were dealt with some surface modification treatments [54,64]. As shown in *Electrospun superhydrophobic structures inspired by nature* section, the LBL assembly as a modern surface modification technique has displayed its advances in fabricating superhydrophobic surfaces. In this section, we will focus on other important techniques reported in the past few years to construct rough surfaces and subsequent modifications of the surface chemistry, which mainly include applying low surface energy materials, plasma and hydrothermal treatments on pre-formed textured fiber surfaces.

Surface modification with low surface energy materials

Electrospinning is a powerful technique to make ultrafine fibers and has also been found to provide sufficient surface roughnesses for superhydrophobicity [24,48,49]. Engineering superhydrophobic surfaces by modifying electrospun fibers with low surface energy materials, decouples the surface wettability from the bulk properties of the materials and enlarges potential applications of superhydrophobic surfaces [4]. This two-step process takes advantage of the intrinsic roughness of electrospun fibrous membranes and relieves the requirement of low surface energy for the fiber composition, since this is now provided by the low surface energy hydrophobic coating. The selection of materials for the electrospun fiber substrate can therefore be based on other performance criteria, such as toughness or thermal stability [42,50]. The conformal nature of the coating and its nanometer-scale thickness ensures that the surface retains the desired fiber-like texture. Up to now, a number of hydrophobic coatings have been modified on electrospun fibers to make a superhydrophobic surface including PPFEMA [84], PFOTS [85], FDTS [66] and FAS [14,21,22].

As one typical example of this approach, Ma et al. [84] reported an effective method to produce superhydrophobic fabrics by combining electrospinning and initiated CVD. PCL was first electrospun and then coated with a thin layer of hydrophobic PPFEMA by CVD. The hierarchical surface roughness inherent in the PCL electrospun mats and the extremely low surface free energy of the coating layer obtained by CVD provided stable superhydrophobicity with a WCA as high as 175° and a threshold sliding angle less than 2.5° for a 20 mg droplet. Additionally, they further investigated the effect of fiber morphology on the hydrophobicity and found that thin fibers having a high density of beads are more hydrophobic than thicker, bead-free fibers. Recently, Pisuchpen et al. [85] reported an alternative multi-step process to construct a superhydrophobic fibrous surface, which was achieved by the reaction of poly(vinyl alcohol) (PVA) fiber mats with multiple cycles of $SiCl_4/H_2O$ treatment followed by silanization with PFOTS. The $SiCl_4/H_2O$ treatment maintained the physical integrity of the PVA fibers and thus yielding PVA–silanol fiber mats. They obtained a superhydrophobic fibrous membrane with WCA of 168° and hysteresis of 0°. The control of wettability with such a facile, cost-effective approach offers the possibility for further exploration of this nanofabrication method for applications in nanowetting, nanoprinting, and nanocoating.

Plasma treatment

Plasma treatment have been regarded as a versatile and effective method for modifying the surface properties or introducing desired chemical groups at the surface of a material without affecting its bulk properties [53,54]. Recent works have shown that plasma treatments could be applied to polymers [86], carbon nanotubes [87], or silicon [88] substrates for fabrication of engineered materials with controlled wettability. Superhydrophobicity of electrospun fibrous membranes can also be produced by surface plasma treatment [53,89]. For instance, Yoon et al. [53] have demonstrated that the hydrophobicity of PHBV fibrous membranes was further improved through treatment of a CF4 plasma. One year later, they prepared a superhydrophobic surface by surface modifying electrospun lotus-leaf-like micro/nanofibrous cellulose triacetate (CTA) membrane (Fig. 10a) with the CF4 plasma [89]. Fig. 10b and c shows the AFM images of the surface of the CTA mat before and after plasma treatment. As shown in Fig. 10a, the non-treated electrospun CTA mat had a rough surface resembling a lotus-leaf, which presents a WCA of 142°. The WCA of the CTA mat reached as high as 153° after plasma treatment for 60 s, which could be attributed to the introduced fluorine atoms onto the CTA fiber surface through the plasma treatment. As the plasma treatment time was further increased from 60 to 300 s, the WCA of the CTA mats gradually decreased, because the surface etching effect caused by excessive plasma treatment became dominant, resulting in a decrease in the surface roughness and fluorine content.

As mentioned above, superhydrophobic surfaces could be obtained by surface modification of electrospun fibers with gaseous CF4 plasma. A question may come to mind, how water behaves when the electrospun fibrous membranes were treated by plasma using other gases without fluorine atoms? Fortunately, Martins et al. [90] answered this question. They compared the WCA between untreated (Fig. 10d) and plasma (Ar or O_2)-treated electrospun PCL nanofibrous membranes, finding a decrease in the hydrophobicity of plasma-treated meshes, particularly in the O_2-treated ones.

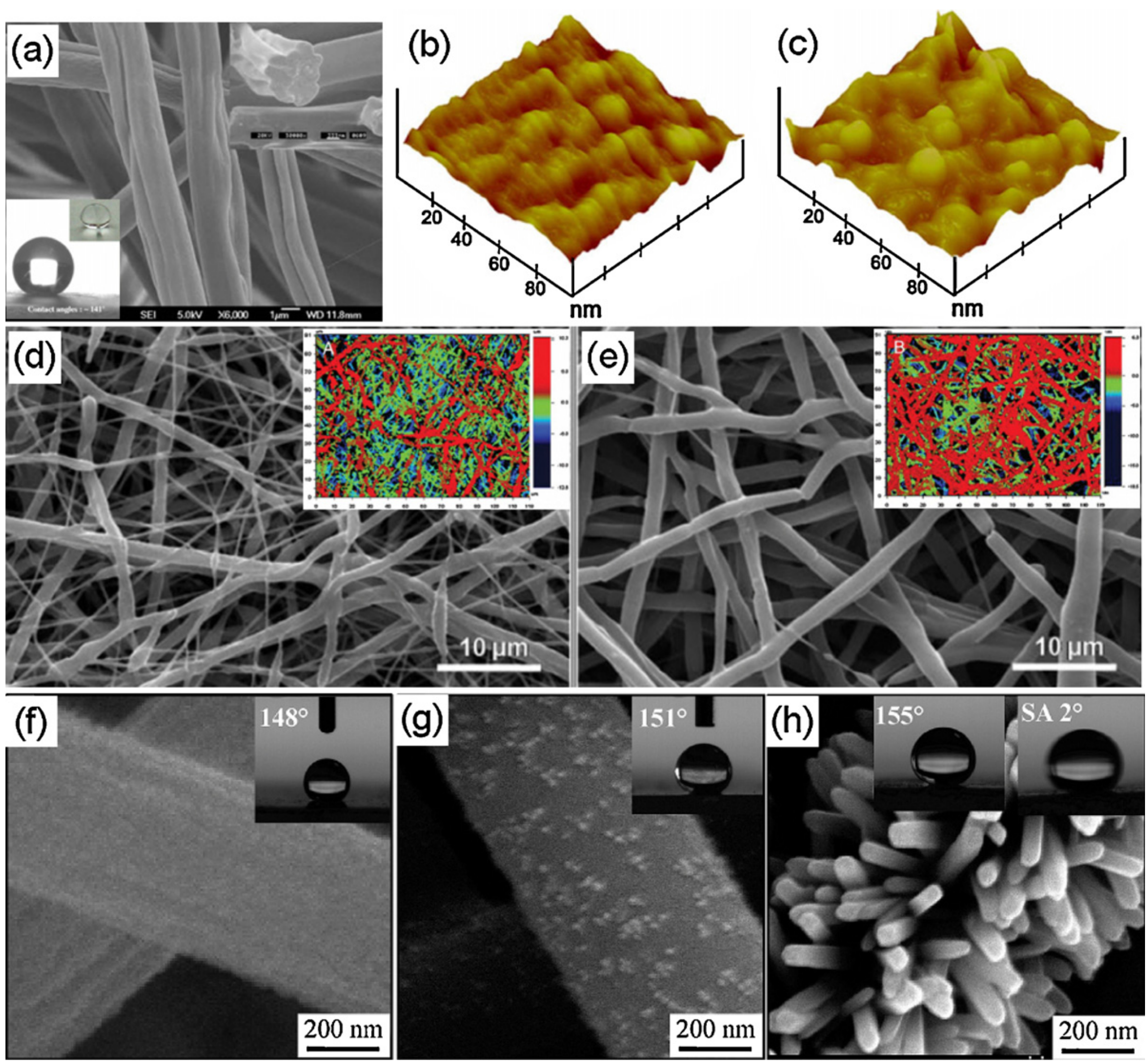

Figure 10 Surface modification of electrospun nanofiber by plasma treatment. (a) SEM image of CTA fibrous membranes. Inset shows the water droplets on CTA fibers. (b and c) AFM images of CTA fibrous mats with various plasma treatment times: (b) 0 s and (c) 60 s. (d and e) SEM images of untreated (d) and plasma-treated (e) PCL NFMs. Insets show the corresponding optical profilometry images. (f—h) SEM images of titania nanomembranes after hydrothermal treatment for (f) 0 min, (g) 60 min, and (h) 120 min.
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The O_2-plasma treatments induced melting of the thinner nanofibers (Fig. 10e) as well as the decreasing of surface roughness, which could also be demonstrated by optical profilometry images.

In fact, plasma treatment on electrospun nanomaterials is a complex process, which can be affected by a lot of factors, such as kinds of plasma, treatment time, the real contact area, surface chemistry, and surface roughness [52—54]. Accordingly, investigation about the fabrication of electrospun superhydrophobic surfaces by plasma treatment is just beginning. Nonetheless, plasma treatment provides an excellent tool for subtly regulating and constructing nanostructured surface on different types of materials, thus could be effectively adapted to many practical applications where surfaces with extreme wetting properties could be exploited [88].

Hydrothermal treatment

As a recently developed technique, the hydrothermal synthesis has been established as an efficient bottom-up route for fabricating functional materials with different patterns and morphologies [91]. Combining electrospinning technique with hydrothermal process, various kinds of nanofibers with versatile hierarchical structures such as firecracker-shaped ZnO/polyimide hybrid nanofibers [32], cedar leaf-like Ag nanostructures [92], and hierarchical TiO_2 membranes [67] have been prepared. Recent studies have also demonstrated that hydrothermally treated electrospun nanofibers show good superhydrophobic properties [67]. Tang et al. [67] constructed a stable superhydrophobic surface by surface modifying electrospun hierarchical TiO_2 membrane (Fig. 10f) with hydrothermal treatment. Titania membranes were subjected to hydrothermal treatment in a $Ti(OBu)_4$ acidic solution for 60 and 120 min. As shown in Fig. 10g and h, nanoparticles of 20—30 nm in size were developed on the fiber after 60 min of hydrothermal treatment surface (Fig. 10g) while the nanoparticles grew along the perpendicular direction of fibers and became rod-like crystals after 120 min of hydrothermal treatment and showed a further enhanced self-cleaning property with WCA of 155° (Fig. 10h). Hydrothermal treatment provides access to generate impressive nanomaterials with reasonable shape and size; an open problem still exists in the field, that is, hierarchical structures with better superhydrophobic property obtained through surface modification of electrospun fibers generally lead to worse mechanical integrity. Only after solving this challenge, this technology may find greater use in fabrication of robust superhydrophobic materials.

Electrospinning hydrophobic materials

Roughening hydrophobic materials (WCA > 90°) through electrospinning provides a one-step strategy to prepare superhydrophobic surfaces. So far, many types of relatively low surface energy materials including fluorinated materials [87,88], PS [47,50], poly(dimethylsiloxane) (PDMS) [93], polyhedral oligomeric silsesquioxane (POSS) [57,58], PHBV [94], and methyltriethoxysilane [95], have already been electrospun into fibers solely or blended with other materials to make a superhydrophobic surface. Here, we give a brief look into the topic of recently developed superhydrophobic surfaces by roughening low surface energy materials through electrospinning.

Fluorinated materials are of particular interest as self-cleaning surfaces or stain-resistant textiles due to their extremely low surface energies [96]. Roughening these materials could lead to superhydrophobicity directly. Singh et al. [97] report the electrospinning of highly fluorinated poly[bis(2,2,2-trifluoroethoxy)phosphazene] to form nonwoven mats with high surface hydrophobicity. The contact angle increased with a decrease in fiber diameter and reached a ''superhydrophobic state'' as both beads and fibers were formed on the surface of the spun mats. The extremely high hydrophobicity of these surfaces is a combined result of surface enrichment with fluorinated units together with the inherent surface roughness associated with an electrospun mat. Agarwal et al. [98] have demonstrated the superhydrophobic surfaces by one-step electrospinning of fluorinated homopolymers and copolymers of 2,3,4,5,6-pentafluorostyrene. Additionally, it is worthwhile to point out that many fluorinated materials cannot be used directly but linked or blended with other materials (which are often easy to roughen) to make superhydrophobic surfaces due to their limited solubility [99]. For example, Islam et al. [100] prepared a superhydrophobic fibrous membrane by electrospinning the fluorinated silane functionalized pullulan. Similarly, superhydrophobic PVdF membranes with a WCA up to 156° were prepared by the electrospinning of the fluorinated silane functionalized PVdF [101]. Acatay et al. [50] obtained an even higher contact angle, 167°, for a superhydrophobic film consisting only of clustered polymeric particles by electrospraying low molecular weight (LMW) poly(acrylonitrile-*co*-R,R-dimethyl-*m*-isopropenylbenzyl isocyanate) (poly(AN-*co*-TMI)) with a perfluorinated linear diol (Fig. 11a). The applications for this particle-only morphology are expected to be significantly limited by their lack of adequate mechanical integrity. Superoleophobic surfaces have attracted much attentions due to their potential applications for self-cleaning and antifouling from biological and organic contaminants in both air and water [1,102,103]. Through appropriate combination of re-entrant curvature and suitable alteration of the solid surface energy, Tuteja et al. [104] obtained omniphobic surfaces with beads-on-strings morphology by electrospinning polymethyl methacrylate (PMMA) solution containing 44.4 wt% fluorodecyl POSS, which repel a range of polar and nonpolar liquids (Fig. 11b) such as methanol, octane, and pentane (Fig. 11c).

Another well-known material with low surface energy is PS, which has been electrospun by several groups to make superhydrophobic surfaces [9,47,50,57]. Jiang et al. [47] reported a contact angle of 160.4° for a superhydrophobic PS film consisting of micrometer-sized particles of PS embedded within a fibrous matrix obtained by electrohydrodynamic spraying and spinning of dilute polymer solutions. Recently, our group proposed a simple method to produce a highly porous superhydrophobic surface of PS by controlling the distribution of silica nanoparticles in porous fibers. WCA up to 156.7° was obtained by transferring silica nanoparticles to the fiber surface to form nanostructured papillae (Fig. 7c) [105].

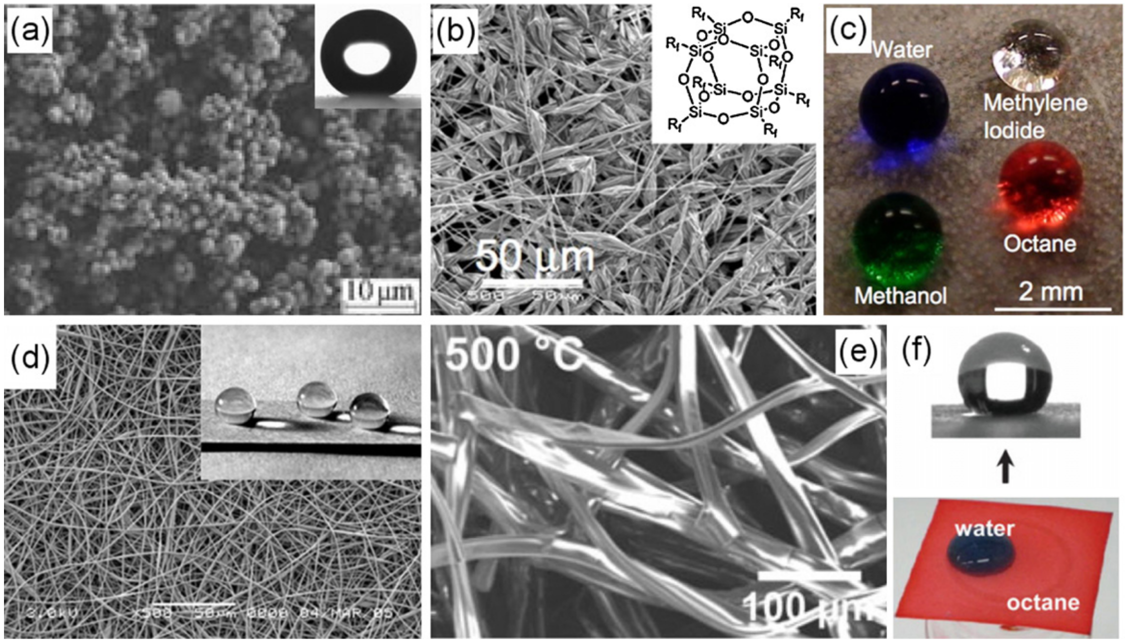

Figure 11 Superhydrophobic surfaces by roughening hydrophobic materials through electrospinning. (a) SEM image for electrospun film of LMW poly(AN-*co*-TMI) with viscosity of 51 mPa s. (b) SEM image of electrospun fluorodecyl POSS—PMMA membranes. The inset shows the molecular structure of fluorodecyl POSS molecules. The alkyl chains (R_f) have the molecular formula $-CH_2CH_2(CF_2)_7CF_3$. (c) Droplets of water, methylene iodide, methanol, and octane on a lotus leaf surface covered with electrospun fluorodecyl POSS—PMMA membranes. (d) SEM image of electrospun PS—PDMS fibrous membrane and the droplets on it. (e) SEM image of electrospun MTES fibrous webs after heat treatment at 500 °C. (f) Water droplet profiles on the MTES fabric used for the separation of water (dyed with methylene blue) and octane (colored with Oil Red O) mixture.

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Apart from these predominant hydrophobic materials (fluorinated materials and PS), PDMS has also been widely used for constructing superhydrophobic surfaces due to its intrinsic deformability and hydrophobic property [4,106,107]. But forming solid fibers comprising solely of linear PDMS is not possible, due to its low glass transition temperature [4]. An alternative way to exploit the low surface energy of PDMS is to use a block copolymer such as poly(styrene-b-dimethylsiloxane) (PS—PDMS). For instance, Ma et al. [93] fabricated a superhydrophobic fibrous membrane by electrospinning a PS—PDMS block copolymer blended with PS homopolymer (Fig. 11d). The superhydrophobicity with WCA of 163° was attributed to the combination of enrichment of PDMS component on fiber surfaces and the surface roughness of the electrospun fibrous membranes.

Recently, multifunctional superhydrophobic surfaces have been widely pursued for potential applications in interdisciplinary technological fields [95]. Methyltriethoxysilane (MTES), as an organically modified silicate (ORMOSIL) precursor, is a promising candidate for generating flexible organic—inorganic hybrid materials with multifunctionalities and thermal stability [95,108]. Lim et al. [95] demonstrated multifunctional superhydrophobic surfaces through creating hierarchically electrospun fibrous structures from MTES with low surface energies (Fig. 11e). Such fascinating fibrous webs were prepared by a combination of sol—gel chemistry of ORMOSILs and electrospinning techniques. The electrospun hybrid fabrics maintained superhydrophobicity even after heat treatment at 500 °C, indicating strong thermal wetting stability. Additionally, they demonstrated that superhydrophobic sheets may be appropriately employed not only as high-performance automobile air filters, but also as oil—water separation membranes (Fig. 11f).

Smart responsive micro- and nanofibrous surfaces

In the preceding sections, we have summarized the progress in the fabrication of superhydrophobic fibrous surfaces. This section will focus on current state-of-the-art research on the switchable wettability of fibrous surface. Controlling the wettability of a solid surface has aroused great interests because of its myriad applications, ranging from self-cleaning surfaces to microfluidics to biomedicine [109,110]. Chemical composition and surface topography are the two key factors in the wettability of solid substrates. Recently, a variety of stimuli-responsive, smart, interfacial materials that can switch between superhydrophobicity and superhydrophilicity have been demonstrated by versatile methods, including light-irradiation, use of an electric field, thermal treatment and treatment with solvent, which can change the surface conformation and/or morphology of stimuli-sensitive materials and thus lead to the change of surface wetting behavior [110,111]. Such smart surfaces can find wide applications in functional textiles, intelligent microfluidic switching, controllable drug release, sensors, and thermally responsive filters [112]. Not surprisingly, the induced topographic nanostructure roughness might intrinsically contribute to the stimuli-responsive wettabilities. Among the various approaches to fabricate such responsive surfaces such as surface-initiated atom-transfer radical polymerization, hydrothermal approach, self-assembled monolayers, electrochemical deposition, and LBL technique, electrospinning has emerged as a very attractive approach with low cost and high efficiency [112,113].

Thermo-responsive wettability

Temperature can trigger change in chemical compositions and/or surface roughness of thermo-sensitive compounds, and hence it is considered a promising external stimulus to easily alter the surface wettability [111]. Poly(N-isopropylacrylamide) (PNIPAAm) is one of the most popular thermo-responsive materials with a lower critical solution temperature (LCST) of about 32—33 °C in water [112,114]. Below the LCST, the hydrophilic C=O and N—H groups in the PNIPAAm chain interact easily with water molecules to form intermolecular hydrogen bonding, which results in an extended brush structure displaying hydrophilicity. But above the LCST, the PNIPAAm chain is more favorable to form intramolecular hydrogen bonding, thus the polymer condense themselves and precipitates out of the aqueous solutions (Fig. 12a) [41,112,115].

As for rough substrates containing PNIPAAm, thermo-dependent experiments indicated that thermo-responsive wettability was greatly improved by surface roughness, which exhibits that thermo-responsive switching between superhydrophilicity and superhydrophobicity can be realized by sufficient surface roughness of the substrate [43]. Therefore, engineering PNIPAAm into micro- and nanostructures through electrospinning is a concern. Due to the poor electrospinnability of PNIPAAm, Wang et al. [113] used PS as template and prepared PNIPAAm/PS composite fibrous membranes by electrospinning. By altering the concentration of the polymers, the wettability of the fibers could be easily fine-tuned. The resultant electrospun fibrous membranes exhibited reversible superhydrophilicity and superhydrophobicity by changing the temperature from 20 °C to 50 °C (Fig. 12b). The addition of cheap PS could generate tailored micro/nano hierarchical surface structures and notably lower the cost of the surface but would not influence its switchability. In a similar study, Gu et al. [112] utilized poly(L-lactide) (PLLA) as template and fabricated PNIPAAm/PLLA nanofibrous films, which also exhibited good thermo-responsive switchable wettability. Recently, Chen et al. [41] for the first time achieved the fabrication of core—sheath structured PCL/PNIPAAm nanofibers by single-spinneret electrospinning and demonstrated the thermo-responsive wettabilities of the fibrous membranes with the temperature changing from 20 to 40 °C. Due to the versatility of the electrospinning method, we can expect

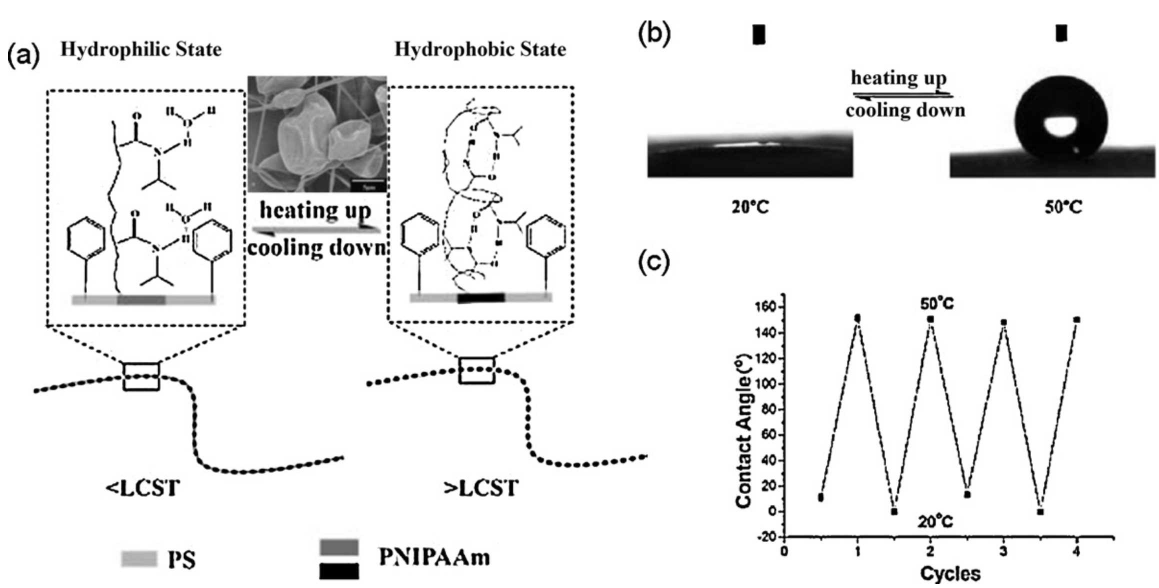

Figure 12 (a) The diagram of the molecular mechanism of the thermally responsive wettability of the PNIPAAm/PS composite films. PS mainly formed the fabric structures of the composite films, while reversible formation of intermolecular and intramolecular hydrogen bonding of PNIPAAm below and above the LCST exhibit the thermally responsive wettability of the composite films. (b) Photographs of water-droplet shape on the PNIPAAm/PS composite film. It shows thermo-responsive properties that could switch between superhydrophilicity at low temperature (20 °C) and superhydrophobicity at high temperature (50 °C). (c) Reversibility of WCA transition on the PNIPAAm/PS composite film III at two different temperatures. Half cycles: 20 °C; integral cycles: 50 °C. Reprinted with permission from [113]. ©2008 Wiley-VCH Verlag GmbH & Co.

that this technique could be readily extended to produce other stimuli-responsive surfaces.

Light-responsive wettability

In recent years, the investigation of light-induced smart surfaces with controllable wettability has attracted extensive attentions in surface science [116]. A particularly fascinating possibility is provided by light-responsive materials allowing a remote and accurate operation that can readily be focused into specific areas of applications. The photo-response of these materials is based on the photoisomerization of constituent molecules that undergo a large conformational change between two states in response to the absorption of light at two different wavelengths [117]. Besides some commonly used inorganic semiconductor oxides, such as TiO_2, ZnO, SnO_2, WO_3, V_2O_5, and Ga_2O_3, organic compounds can also show the behavior of light-responsive wettability [43,116]. For example, azobenzene, a typical photoresponsive organic material, undergoes a reversible conformational transition between *cis* and *trans* isomers under UV and visible irradiation. Chen et al. [117] first fabricated light-responsive electrospun azobenzene-modified PCL (PCL-azo) nanofibers (Fig. 13), which could reversibly change between two wettability states with UV/vis irradiation. The changes observed upon UV irradiation were due to the reversible *trans*-to-*cis* isomerization of the azobenzene groups. An increased dosage of azobenzene on the surface, which could be confirmed by time-of-flight secondary ion mass spectrometry (ToF-SIMS) (Fig. 13b), induced a larger lowering of the surface free energy upon *trans*-to-*cis* isomerization and consequently a lower WCA. Different nanofibrous membranes with different concentrations of BP-azo tethered to PCL were produced by electrospinning and found that mat III

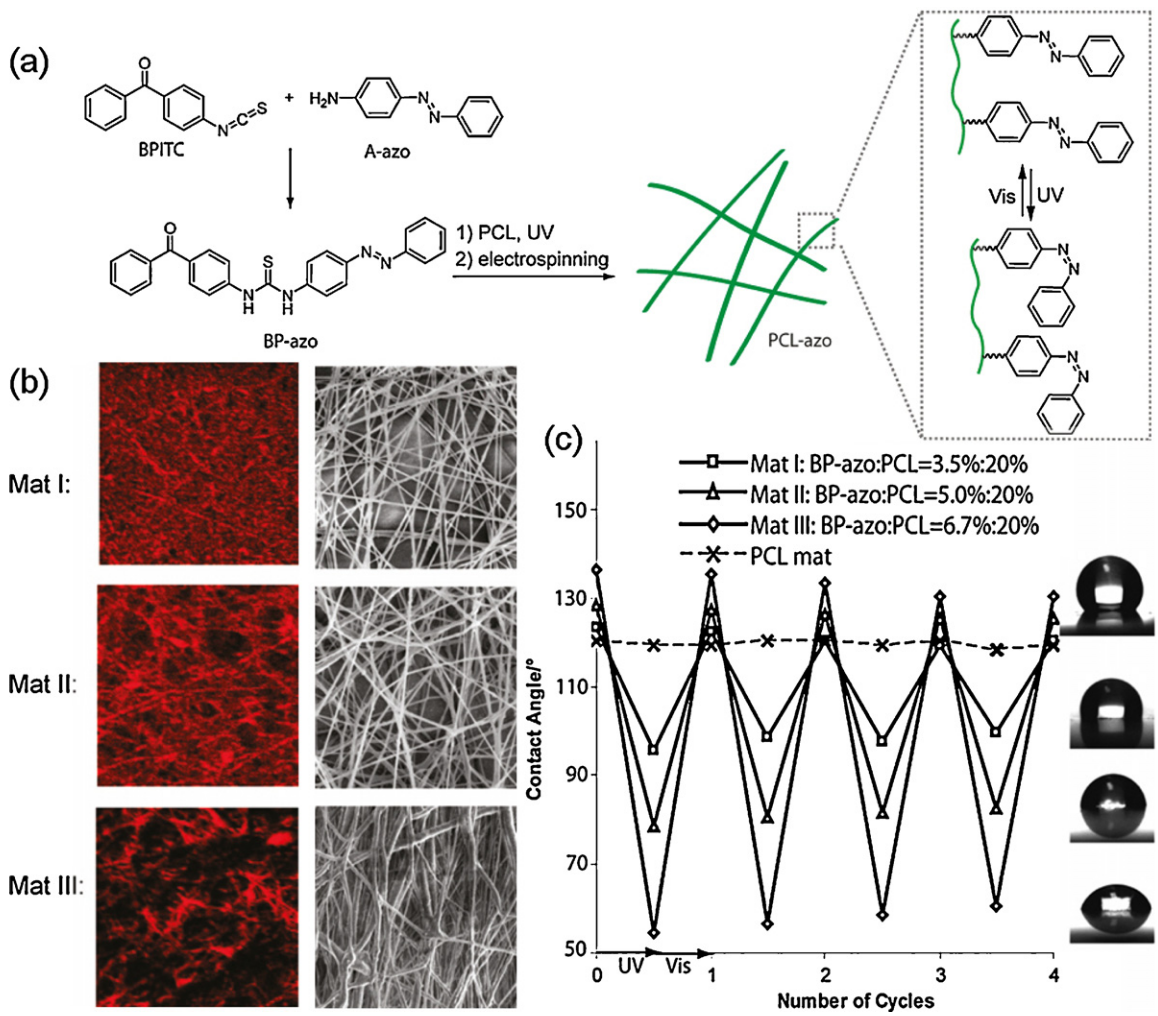

Figure 13 (a) Schematic illustration of electrospinning of PCL-azo and the produced light-responsive nanofibers. (b) ToF-SIMS chemical images and SEM images of the nanofibrous mats I—III. (Left) Azobenzene fragment ion images; (right) SEM images. Area: $20\,\mu m \times 20\,\mu m$. (c) Photographs of water droplet shape and on mats I—III, which show that photoresponsive wettabilities could reversibly switch between hydrophobicity and hydrophilicity upon UV/vis irradiation. PCL mat without azobenzene displayed no photoresponse but hydrophobic nature.
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(BP-azo/PCL = 6.7%/20%) showed the most significant static WCA change; the WCA of mat III decreased from $132.2 \pm 2.8^\circ$ to $53.1 \pm 3.2^\circ$ upon UV irradiation (Fig. 13c).

Chemical dual-responsive wettability

Although many stimuli-responsive surfaces have been fabricated exhibiting reversible wettability, they are responsive to only one kind of external stimuli. In some applications, dual/multiple-responsive materials are also necessary, especially in drug delivery field [116]. Recently, Zhu et al. [118] reported the preparation of a chemical dual-responsive surface wettability, which can be easily triggered by changing pH value or redox properties of the solution. Such smart surfaces were obtained by polymerizing PANI onto the electrospun PAN fibers, thus forming PANI—PAN coaxial nanofibrous membranes. Reversible switching between superhydrophilicity and superhydrophobicity was achieved both in a relatively wide pH (from pH 1.02 to 13.07) and for oxidizing droplet with $2.51\,\mathrm{mol\,L^{-1}}$.

Janus nanofabrics

Recently, it has become customary to call a fabric with two faces a ''Janus'' fabric, named after Janus, the God of beginnings and transitions in ancient Roman religion and mythology, who was depicted as having two opposite and distinct faces [119]. Janus nanofabrics present a number of fascinating properties related to their asymmetric structures. Only recently has this type of fabric been of interest, and thus only a few literatures about Janus nanofabrics have been reported [120]; however, it is really a prospectively multifunctional entity especially due to their unique wetting characteristics [46,120,121]. Lim et al. [120] demonstrated the fabrication of biphasic Janus fabrics by electrospinning PAN-TEOS fibers onto the thermal hydrolyzed (200 °C in air) electrospun PAN-TEOS fibrous layer (Fig. 14b). The resultant Janus fabric displayed antisymmetric wetting behavior: on one side, the electrospun PAN-TEOS mat exhibited superhydrophobic properties, with a WCA of 151.2° (Fig. 14c), on the other side, the initially superhydrophobic PAN-TEOS sheet on the opposite side of the fabric was converted to a superhydrophilic surface (WCA of 0°, Fig. 14a) through hydrolysis of the surface functional groups induced by the thermal treatment. This robust and tailored strategy combined the production of hierarchical geometric architectures by electrospinning and the superhydrophobic-to-superhydrophilic wetting transition induced by thermal hydrolysis of the PAN nanofibers, which opens a new route for the design and development of functional smart fabrics from inexpensive and commercially available polymers.

Conclusions and outlook

This review provides an overview of recent developments in controlled fabrications of well-defined bio-inspired superhydrophobic surfaces of nanomaterials via electrospinning technique. Particular attention is devoted to the strategies for fabricating rough superhydrophobic surfaces inspired from nature, surface modification of rough electrospun nanomaterials and directly electrospinning the low-surface energy materials. The potential commercial importance of these surfaces for everyday applications ranging from building materials to apparel and for technical applications, and some commercial products have started, e.g. non-stick pans, superhydrophobic textiles and self-cleaning coatings [8].

Recent years have witnessed a rapid expansion of research on fabricating superhydrophobic micro- and nanofibrous surfaces as documented in this review. Biomimetics is a newly emerging interdisciplinary field in materials science, nanotechnology, biology and engineering [2]. The biomimetic and bio-inspired approaches to materials are some of the most promising scientific and technological challenges in the coming years. Matching the material's structure and function to the desired practical condition is of significant importance, which of course is sometimes a complicated process [15]. Revealing the nature's secret and further subtracting the beautiful mechanism can render original inspirations, help people to guide the scientific research and bridge the gap between academic research and practical application [16].

From the fundamental points, we conclude that fabricating a surface with superhydrophobicity or superhydrophilicity requires a rough surface structure. However, the surfaces will show worse mechanical stability with the increasing roughness, which is the main barrier preventing biomimetic superhydrophobic surfaces applying into industry at the current stage [122]. Therefore, the question of how to find the balance or how to enhance the surface

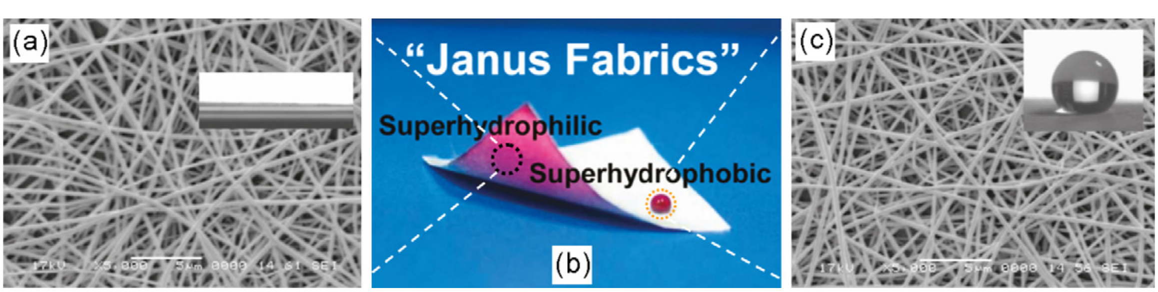

Figure 14 Biphasic Janus nanofabric. (a and c) SEM images and contact angles of the electrospun PAN-TEOS nanofibrous mats (a) after and (c) before heat treatment, respectively. (b) Photograph of the free-standing biphasic Janus fabric displaying antisymmetric wetting behavior.
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mechanical properties withholding the surface superhydrophobicity will be an important challenge in the future. Fortunately, several attempts have emerged that promise to bridge the gap, for instance, electrospun nanofibrous materials offer some particular superiority such as ease of formation, mechanical integrity, and self-supporting structure, which provide a potential solution to solve this problem [123—125].

Another important issue that hampers the industrial applications of the superhydrophobic surfaces is the contamination from liquids other than water. Therefore, surfaces that are highly water-repellent, oil-repellent (superoleophobic) and even any liquid-repellent (omniphobic) [104] are of particular significance. Thanks to the efforts of McKinley and Cohen's groups, unique re-entrant texture surfaces based on electrospun fibrous materials come out, which exhibit extreme resistance to wetting from a number of liquids with low surface tension. Additionally, the concept of re-entrant geometry particularly relative to fibrous materials help us further understand the connection between the parameters of the models and the measurables of experiment for the cases of nonwoven, horizontally aligned and vertically aligned fibers [19].

Although many challenges are on the way, electrospinning possesses the ability to the fabrication of fibrous nanomaterials with controllable compositions and structures, which mimic the nature and thus show great potential for constructing numerous superhydrophobic surfaces. We believe the continuous efforts on exploration of biomimetic research through the intensive collaboration of scientists from various disciplines will vigorously push the field forward. Furthermore, we anticipate that electrospinning technique will be a comparatively important driving force for the development of superhydrophobic field and will bring more exciting future for this field.

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