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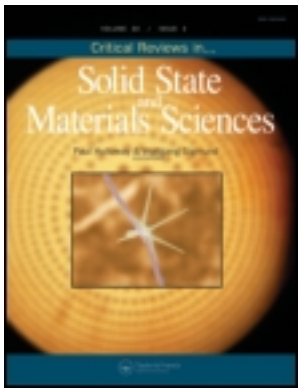

Critical Reviews in Solid State and Materials Sciences
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/bsms20

Biomimicry via Electrospinning

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Available online: 07 Jun 2012

To cite this article: Jinyou Lin, Xianfeng Wang, Bin Ding, Jianyong Yu, Gang Sun & Moran Wang (2012): Biomimicry via Electrospinning, Critical Reviews in Solid State and Materials Sciences, 37:2, 94-114

To link to this article: http://dx.doi.org/10.1080/10408436.2011.627096

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Critical Reviews in Solid State and Materials Sciences, 37:94–114, 2012
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ISSN: 1040-8436 print / 1547-6561 online
DOI: 10.1080/10408436.2011.627096

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Biomimicry via Electrospinning

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Electrospinning, an efficient technique to produce long fibers with micro- or nanoscale diameters, has attracted tremendous interests during past decades. By orchestrating parameters in electrospinning, diverse forms of fibrous assemblies and individual fibers with hierarchical structures can be successfully achieved. Some of these versatile micro- and nanostructures display a remarkable resemblance to the materials and objects existing in nature, such as honeycomb, spider webs, extracellular matrix, plant tendril and leaf, etc. The emerging field of biomimicry enables one to mimic biology or nature to develop novel nanomaterials as well as to improve processes for materials via electrospinning. In this review, we present a full panorama of recent studies on biomimicry via electrospinning, and highlight some of biomimicked one-dimensional nanomaterials as well as their functions and applications to date.

Keywords electrospinning, biomimicry, biomimetics, electrospun fibers, hierarchical structures

Table of Contents

1. INTRODUCTION 95

2. ELECTROSPINNING TECHNOLOGY—AN OVERVIEW 95
2.1. History of Electrospinning 95
2.2. Processing of Electrospinning 96

3. BIOMIMETIC PROCESS VIA ELECTROSPINNING 97

4. BIOMIMICRY VIA MANIPULATING FIBER ASSEMBLIES 98
4.1. Bamboo Leaf 99
4.2. Feather 99
4.3. Honeycomb 100
4.4. Extracellular Matrix 101

5. BIOMIMICRY VIA MANIPULATING INDIVIDUAL FIBER STRUCTURES 102
5.1. Lotus Leaf 102
5.2. Silver Ragwort Leaf 103

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5.3. Plant Tendril 104
5.4. Soap-Bubble and Spider Web 106
5.5. Polar Bear Hair 108

6. APPLICATIONS INSPIRED FROM NATURE 110
6.1. Self-Cleaning Materials 110
6.2. Tissue Engineering 110
6.3. Sensors 110
6.4. Catalysis and Others 110

7. SUMMARY 110

ACKNOWLEDGMENTS 111

REFERENCES 111

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1. INTRODUCTION

After billions of years' stringent evolution and natural selection, nature has developed some materials and objects that are endowed with fascinating structures with unique properties and functions, such as high strength, self-cleaning, structural colors, thermal insulation, dry adhesion and so on.[1,2] The understanding of these properties created by nature may give us new insights into the imitation and production of new materials and processes. For instance, the idea of fishing nets may have originated from spider webs; the robust hexagonal honeycomb may have led to its applications in lightweight structures in airplane.[3] Copying, adaptation or derivation from biology is referred to as 'biomimicry.'[4] The term 'biomimetics' introduced by Schmitt in 1969,[5] and originates from the Greek word biomimesis.[6] Biomimetics can be defined as the investigation of the formation, structure or function of biologically produced substances and materials and biological mechanisms and processes especially for the purpose of synthesizing similar products by artificial mechanisms which mimic natural ones.[7] The emerging field of biomimetics allows human to mimic nature to exploit nanomaterials, nanodevices, and processes which provide desirable properties.[7]

Diverse features found in nature's objects are on the nanoscale. The major focus on nanoscience and nanotechnology since the early 1990s has provided a significant impetus in mimicking nature using nanofabrication techniques for commercial applications.[1,4] As an increasing hot nanofabrication technique, electrospinning has emerged as a versatile and cost-effective method for producing long continuous fibers with diameters ranging from several micrometers down to a few nanometers by applying a high voltage on a polymer solution or melt.[8–10] For many reasons, electrospinning provides unique opportunities to emulate nature. From the name "spinning," we can imagine a picture in which a spider is spinning its web. The difference may lie in that the electrospinning is induced by the unique electrical power. Thus we can draw an incipient conclusion that the process of electrospinning is biomimetic (details will be discussed in Section 3). Additionally, the building blocks of natural polymer-based nanofibrous membranes at the lowest level of hierarchy (nano to micro) are organic fibers, and many of these are natural. Furthermore, like many natural functional surfaces, the large surface area of electrospun fibrous membranes offers tremendous opportunities to functionalize them.[3] More importantly, electrospun materials exhibit various fascinating morphologies such as bead-on-string, ribbon-like, helical, porous, necklace-like, firecracker shape, rice-grain shape, core-shell, multi-channel tubular, multi-core cable-like, tube-in-tube, nanowire-in-microtube, and hollow structures.[8] All of these attributes lend electrospun fibers more to biomimetic concepts compared with other fibers.

This review will focus on the recent developments on biomimicry via electrospinning, particularly on bio-inspired electrospun nanomaterials as well as their functions and applications. The major part of this review is organized into five sections. In Section 2, we give an overview about electrospinning technology. A brief summary of the bio-inspired electrospinning process is shown in Section 3. Sections 4 and 5 present a comprehensive overview on manipulating fiber structures inspired by nature. Some potential applications associated with biomimicry are highlighted in Section 6. Finally, we provide conclusions about this review and also present personal prospects on the future of this topic.

2. ELECTROSPINNING TECHNOLOGY—AN OVERVIEW

2.1. History of Electrospinning

Electrospinning, also known as electrostatic spinning, is considered as a variant of the electrostatic spraying process which was first found by Bose in 1745.[10] The first devices to spray liquids through the application of an electrical charge were already patented by Cooley and Morton at the beginning of the 20th century.[11–13] In 1914, Zeleny reported that the fine fiber-like liquid jets could be emitted from a charged liquid droplet in the presence of an electrical potential, which is

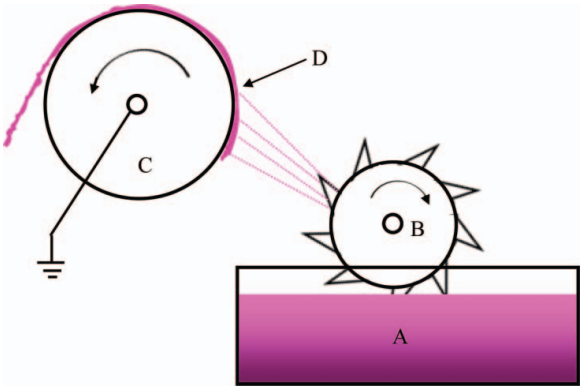

FIG. 1. Formhals' experimental apparatus for producing artificial filaments via electrospinning: (A) spinning solutions are passed into electrical field formed between two electrodes composed of (B) a slender rotating serrated wheel in a pool and (C) a wheel as a collector. The artificial filaments (D) are continuously removed and collected from the rotating collector. (Color figure available online.)

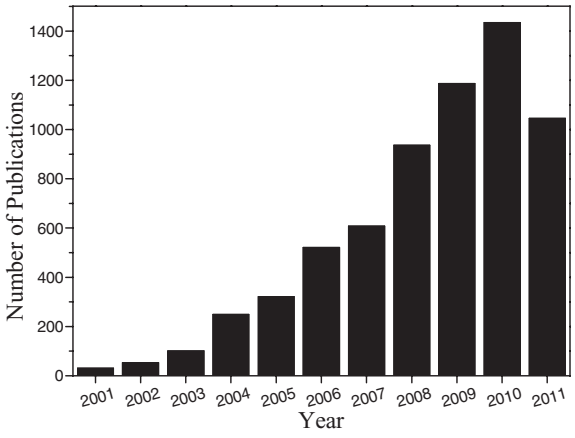

FIG. 2. Schematic representation of the annual number of publications on electrospinning or electrospun during the past decade, following the ISI Web of Knowledge. For 2011, there are already 1046 publications before July 15.

considered to be the origin of principle for the modern needle electrospinning.[14,15] In 1934, a crucial patent, revealing the experimental apparatus for the practical production of artificial filaments using electrical field (Figure 1), was issued for the first time by Formhals.[16] Later on, a series of patents were issued,[17–19] which focused on improvements and modifications on the electrospinning apparatus. In the 1960s, Taylor worked out the instability criteria of spherical liquid droplets subjected to an external electrostatic field.[20,21] Significantly, he obtained the characteristic value of the cone's semi-vertical angle at 49.3°, which was also referred as the "Taylor cone." Then, others applied this work on a wide variety of polymeric systems in preparing electrospun fibers.[22–24]

Despite these early discoveries, electrospinning did not obtain substantial attention until the booming of nanotechnology in the 1990s. Several research groups, especially the Reneker's group, revived electrospinning by demonstrating the fabrication of ultra-thin fibers from various polymers.[25,26] Initialized by the Reneker group, the popularity of electrospinning has increased exponentially in the past decade as clearly reflected from the variation of publication numbers in this filed (Figure 2). Through further investigation of these publications, we can summarize that the development of electrospinning in the recent 10 years are featured in the following six aspects:[27] (i) extensively increased varieties of polymers and composites; (ii) comprehensive understanding of the formation of electrospun fibers; (iii) highly designed structures of electrospun fibers inspired from nature; (iv) the booming of multi-components and inorganic fibers; (v) the transfer of research focus from fabrication to applications including tissue engineering, filtration, catalysis, self-cleaning, drug delivery system, sensors, dye-sensitized solar cells (DSSCs), etc.; (vi) large-scaled production of electrospun fibers by modified electrospinning equipments for commercial use.

2.2. Processing of Electrospinning

In general, a typical electrospinning setup usually consists of three major components (Figure 3a), i.e., a high voltage power supply, a spinneret (a metal needle usually connected with syringe controlled by syringe pump), and a grounded target (as a collector).[28] During electrospinning, the high voltage was applied to the polymer solution, the suspended liquid droplet at the needle tip was highly electrified and the induced charges were eventually distributed over the surfaces. The charged droplet will be subjected to the electrostatic forces into a conical shape.[9] When the applied voltage surpasses the critical value, a thin polymer jet is ejected from the tip of the Taylor cone. The jet follows a direct path towards the grounded target for a very short distance from its origin and reaches a bending instability point, and then the jet begins to whip, as shown in Figure 3a. The charged jet undergoes bending instability combined with solvent evaporation and jet solidification, forming a long and thin fiber in a form of non-woven fabric.[29–31] Additionally, the so-called electrospinning process is closely related to the utilized solution. The ejected jet may break into small droplets or particles due to the Rayleigh instability as a result of low viscosity of solution,[32] which results in the formation of beads-on-string fibers or even micro-spheres. Meanwhile, with an increase of the solution concentration, the resultant fibers are bead-free with a uniform diameter (Figure 3b).

The morphologies and diameters of electrospun fibers are governed by the parameters during electrospinning, which include the solution parameters, the processing parameters, and the environmental parameters.[33] The effects of these parameters on as-spun fibers are summarized succinctly as follows.

Generally, a lower polymer concentration leads to a lower liquid viscosity. Whereas, the fibers become thicker with uniform diameter if more concentrate solutions are used (Figure 3b).[34] For a given concentration, lowering the surface tension of spinning solution favors the formation of continuous fibers with

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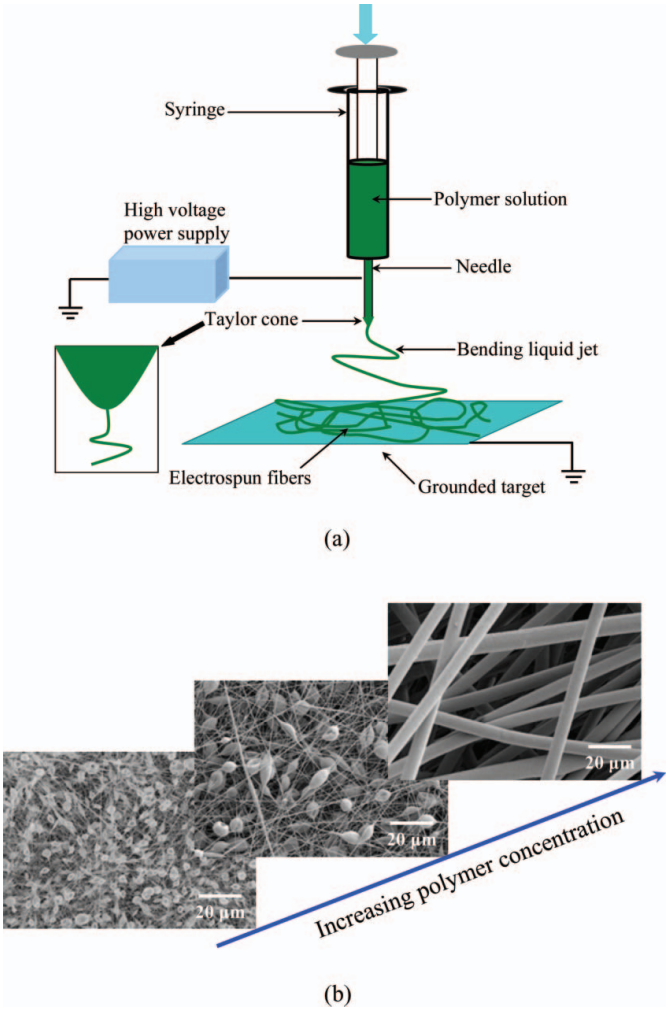

FIG. 3. (a) Schematic illustration of the typical setup for electrospinning. (b) (Scanning electron microscope) SEM images of the electrospun polystyrene (PS) fibers formed from different polymer concentration. (Reprinted with permission from Lin et al.[34] Copyright 2010: American Chemical Society.) (Color figure available online.)

fewer beads.[35] Polymer with a higher molecular weight can be electrospun into continuous and bead-free fibers at a relatively lower concentration, and meanwhile, a high concentration is necessary for forming uniform fibers.[33,36] The conductivity of a solution increases by adding salts, the fiber diameters can be effectively reduced as well as the number of beads.[35,37] The solvent volatility affects the rate of solvent removal from the fluid jet, as well as the phase separation and solidification of the jet. High-volatility solvents are easy to form a porous-surface morphology.[38] Meanwhile, the surface morphology of resultant fibers can also be manipulated by tuning the ratio of solvent mixtures.[34,39]

Sufficiently high electrical field strength is an essential condition for electrospinning. When a stable jet ejects from Taylor cone, an increase of the electrical field strength will enable the Taylor cone retreat into spinneret. Meanwhile, the number of beads will dramatically increase and the distribution of fiber diameters will become much wider.[40,41] Whether the fiber diameters increase or decrease with the electrical field strength depends on the solvent system in electrospinning. Additionally, increasing the electrical field strength can raise the productivity of the resultant fibers. A higher solution flow rate will lead to thicker fibers for a concentrate polymers solution; otherwise, more beads will be formed in the resultant fibrous mats.[36,41] If the working distance is too short, the jet will deposit on the target before dry, resulting in adhesion among the fibers.[42] Furthermore, the effect of working distance on the fiber diameters is closely related to the solution properties.

Usually, electrospinning is conducted at the room temperature in air. When the environmental temperature rises, the conductivity of solution increases while the viscosity and the surface tension decrease. This enables some polymers that failed to be electrospun at the room temperature to be able to be electrospun into fibers.[43,44] For a solution composed of water-soluble polymer and solvent miscible with vapor in air, increasing the relative humidity will lead to the formation of more beads, and in some cases the fibers are adhered to each other due to the residual solvent.[45,46] If the hydrophobic polymer is dissolved in some organic solvent with a high volatility, increasing the relative humidity will increase the number of nano-pores on the fiber surfaces, and for some cases the fiber interior is highly porous due to vapor induced phase separation.[47,48]

3. BIOMIMETIC PROCESS VIA ELECTROSPINNING

In nature, spiders and silk worms can spin continuous fibers by passing aqueous liquid crystalline protein solution through their spinnerets.[49] The resultant fibers exhibit remarkably high strength and toughness, which has attracted tremendous interests of scientists in various disciplines for a long time to trace the mechanism of silk processing in insects and spiders and to produce the high-performance fibers resembling spider silk fiber. Interestingly, many attempts to make synthetic fibers mimicking the native silk resulted in the successful production and commercialization of some polyamide materials such as Kevlar and Nylon, which exhibited a comparable strength but a lower toughness to the dragline silk.[50]

Inspired by native spider silk, many methods have been used to spin the artificial spider silk including the conventional wet-spinning of the regenerated dragline silk and reconstituted *B. mori* silk protein and analogue, however, the comprehensive understanding of the molecular processes occurring during spinning of protein fibers and the investigation of how the spinning conditions to affect the properties of final material have not been fully work-out.[3] Furthermore, it is a mystery that the native silk fibers can be produced with a minimal force by spiders, unlike the man-made fibers formed from its spin solution required a very high pressure or a large drawing force.[51]

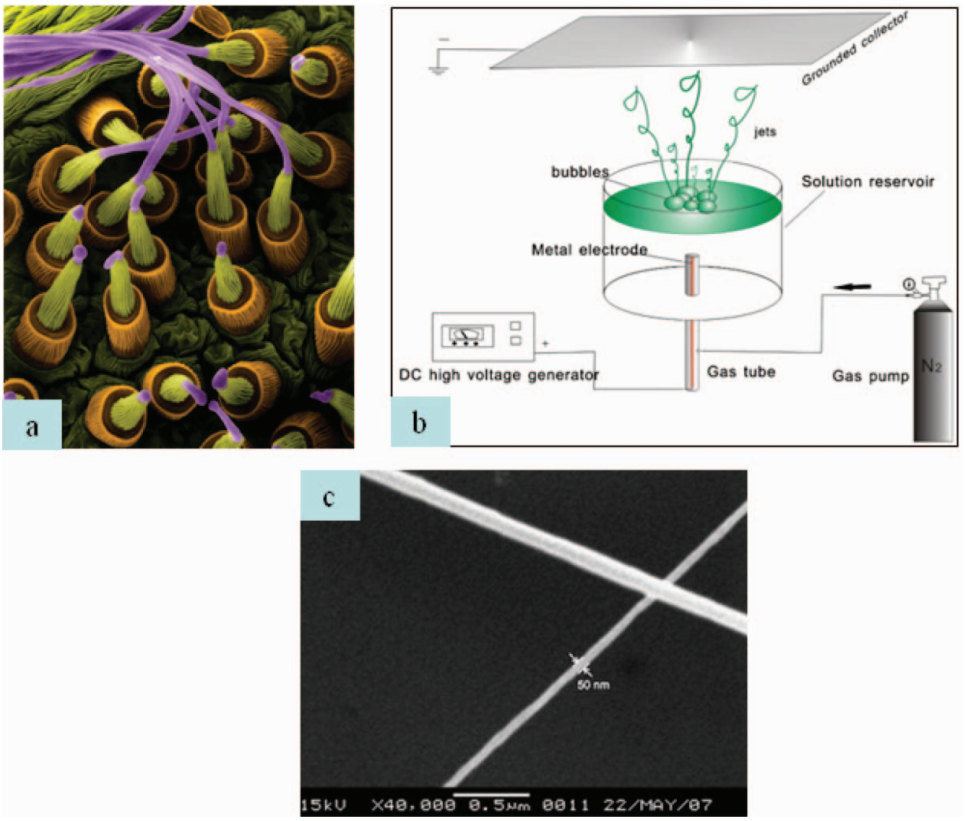

FIG. 4. (a) Spider-spinning process. (b) The experimental setup of the aerated-solution electrospinning. (c) SEM image of the typical resultant fibers. (Reprinted with permission from He et al.[51] Copyright 2008: Elsevier.) (Color figure available online.)

Recently, researchers have revealed that all spiders have silk-producing spinnerets at the end of the abdomen consisting of a great number of nanoscale tubes (Figure 4a), the spin solution can be extruded out and form a bubble at the apex of each tube.[51,52] He et al.[51] confirmed that the surface tension of each bubble was so small such that it could be spun into nanofibers with an awfully small force, either by the spider's body weight or tension created by the rear legs. To mimic this mysterious spinning process, they developed a new spinning system (also known as bubble-electrospinning) to produce nanofibers by ejecting polymer jets from the bubble formed from the highly charged aerated polymer solution (Figure 4b). The mechanism of this spinning process can be described as that the charges accumulated on the bubble surfaces formed from the aerated solution in the presence of an electric field, and a fluid jet ejected from the apex of the conical bubble once the electric field exceeds a critical value needed to overcome the surface tension, subsequently, the jet solidified into nanofiber. Additionally, the minimum diameter of nanofiber produced by this process can reach as small as 50 nm (Figure 4c).[51] This strategy successfully biomimicked the spider spinning process and overcame some shortcomings of traditional electrospinning such as strongly dependent on the solution viscosity.

4. BIOMIMICRY VIA MANIPULATING FIBER ASSEMBLIES

In general, the electrospun fibers are deposited on a target in the form of non-woven fibrous mats, which consists of randomly oriented micro- and/or nanofibers, as shown in Figure 3b. This typical assembly structure of electrospun fibers can be attributed to the jet instability in unique electrospinning process. In the past few years, a great number of novel electrospinning equipments with improved designs or additional setups, such as using a rotating cylinder or disc, two parallel electrodes separated by a gap as collector,[53–55] introducing insulators to grounded collector to influence the fiber deposited position,[56] adding an assistant magnetic field to alter the fiber trajectory in the spinning process,[57,58] have been well developed to alter the resultant fiber assembled structures to obtain the designed fibrous mats with expected structures and functionalities. The controllable fibers deposition endows their assembly with periodic structures exhibiting some unique properties, which broadens the applications of electrospun fibrous mats. Recently, many fascinating structures from nanoscale to macroscale existing in nature have been successfully mimicked via electrospinning technique. Some typically biomimetic structures will be fully discussed as follows. In this section, we will introduce the recent progress in the

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design of biomimetic electrospun fiber assemblies inspired by nature.

4.1. Bamboo Leaf

In nature, some plant leaves are anisotropic surface patterning, such as the natural rice leaf, the lotus leaf margin, and the bamboo leaf,[59–61] resulting in different surface wettability in two directions of these surfaces. Figure 5b shows a water droplet placed on the surface of a bamboo leaf.[61] The water droplet displayed an ellipsoidal shape rather than spherical, reflecting the anisotropic property of the bamboo leaf surface. To mimic the native surface, Wu et al.[61] prepared aligned poly(vinyl butyral) (PVB) fibrous mats by utilizing a modified collector (i.e., two parallel conductive copper strip electrodes separated with a small gap). The resultant fibers were stretched to span across the gap and aligned uniaxially in relatively large areas due to the redistribution of the electric field of the modified collector (Figure 5a). Figure 5c displays a water droplet placed on the biomimetic surface of assembled fiber arrays transferred from collector, and the water droplet exhibits a very similar shape to that on the bamboo leaf. The observation by SEM and atomic force microscopy (AFM) is shown in Figures 5d and 5e, respectively, revealing the micro- and nanostructrures of the biomimetic surface.[61] Benefit from this easy and fast fabrication method, aligned electrospun nanofibers provide a new platform to realize functional surfaces with desired wetting properties on a large scale.

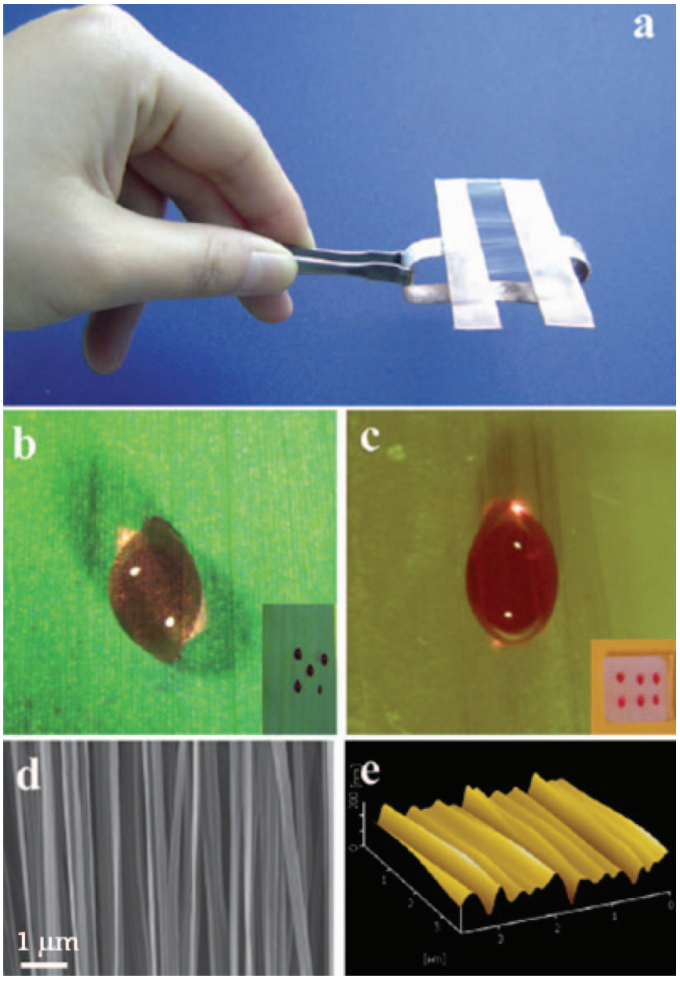

FIG. 5. (a) A digital photograph of the aligned fibers collected between two parallel electrodes. A water droplet set on the surface of (b) a bamboo leaf, (c) a silicon wafer coated by aligned electrospun PVB nanofibers. (d) SEM image of aligned PVB nanofibers. (e) AFM image of the fiber array. (Reprinted by permission from Wu et al.[61] Copyright 2008: The Royal Society of Chemistry.) (Color figure available online.)

4.2. Feather

In addition to the plant leaves, other examples of anisotropy were also found including the pigeon feather, the goose feather, and the duck feather.[61–63] Figure 6 provides the detailed morphology of the pigeon feather and its hydrophobicity.[62] Figure 6a depicts that the feather was separated into two symmetric parts by rachis with a diameter at about 110 μm, and the barbs (about 20 μm) sent forth from rachis with a slant angle about 30° paralleling to each other. The corresponding high-magnification SEM image reveals that there are many barbules (about 5 μm) sent forth from the barbs slantly as shown in Figure 6b. This fascinatingly hierarchical structure contributs to high water contact angles (WCAs) of the pigeon feather (Figure 6b, inset).

Besides pigeon feather, some other waterfowl feathers also have special surfaces with anisotropic wetting properties. Wu et al.[61] studied the WCAs of the goose feather and found that the contact angles viewed in all three directions were different from each other (Figure 7b). This multi-direction anisotropic wetting property was ascribed to the dissymmetry of the microstructure pattern which was very similar with the structure of the pigeon feather. To obtain the fibrous membrane with a feather-like structure, a typical fiber collector was designed by Wu et al. as described in Figure 8a, consisting of a spiculate metal needle perpendicularly with a rectilinear metal strip.[61] The electrospun PVB nanofibers presented a fan-shaped radiating nanofiber pattern with a similar microstructure to a goose feather. The water droplet placed on the artificial surface exhibiting a streamlined shape was depicted in Figure 7c, indicating that the fibrous membrane with an anisotropic wettability in multiple directions was successfully mimicked via altering the nanofibers orientation.

According to the concept of re-entrant geometry proposed by McKinley and Cohen's groups,[63] many natural surfaces, such as various bird feathers and plant leaves, inherently possess re-entrant surface texture, which enables them to support a composite interface with water and thereby exhibit superhydrophobicity. Inspired by re-entrant structured duck feather, they demonstrated the fabrication of re-entrant beads-on-string structured membranes by modifying electrospun polymethyl methacrylate fibrous membranes using polyhedral oligomeric silsesquioxane.

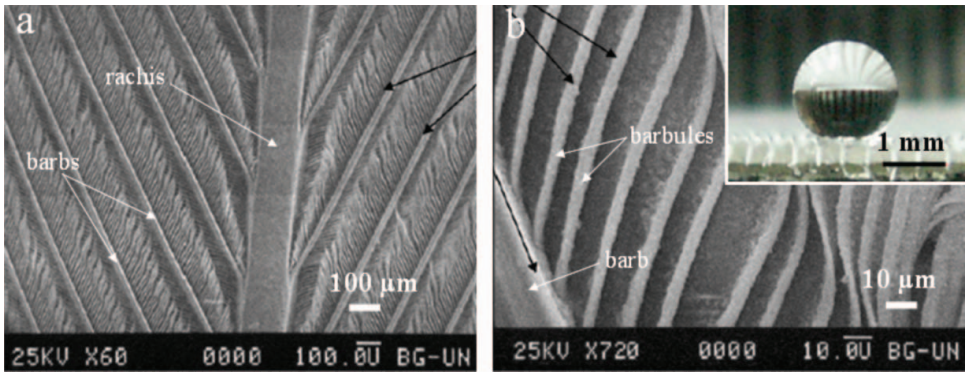

FIG. 6. (a) SEM image of the central part of a feather. (b) SEM image of the pigeon feather structure, inset showed the water drop placed on the edge of the cut feather. (Reprinted with permission from Bormashenko et al.[62] Copyright 2007: Elsevier.) (Color figure available online.)

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The concept of re-entrant geometry especial relative to fibrous materials help us further understand the connection between the parameters of the models and the measurable experiment for the cases of various fibrous structures.[64]

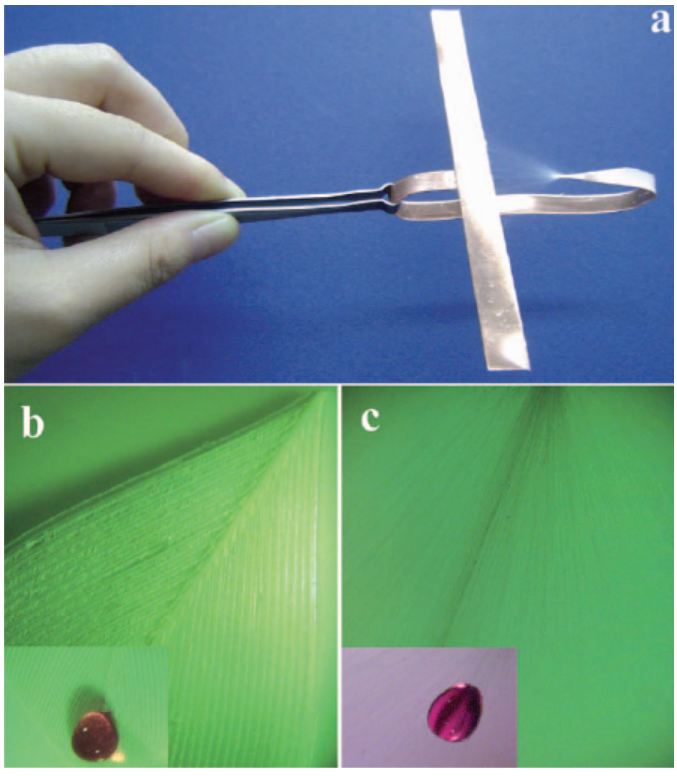

FIG. 7. (a) Digital photograph of fan-shaped radiating nanofiber pattern collected by a spiculate copper needle perpendicular to a rectilinear copper strip. A water droplet set on the surface of (b) goose feather, (c) fan-shaped radiating nanofiber pattern. (Reprinted with permission from Wu et al.[61] Copyright 2008: The Royal Society of Chemistry.) (Color figure available online.)

4.3. Honeycomb

A honeycomb, presented in Figure 8, is composed of hexagonal wax cells constructed by honeybees in their nests to protect their larvae and store honey and pollen. The honeycomb consists of many hexagons due to the hexagon tiles the plane with minimal perimeter per piece area.[65] This typical structure has advantages to adapt nature selection. Alternatively, the term, honeycomb, is also used for man-made materials that resemble it in appearance or structure. Many researches have confirmed that the honeycomb composite materials made of paper, graphite, or aluminum can significantly reduce their weight of components of cars, planes, and spacecraft with little sacrifice in strength.[66]

Self-assembly technique has been used to arrange small components, especially nanoscale objects, into ordered systems or aggregates with desired structures such as monolayers, superlattices, tubes, and honeycomb micro-porous films very easily at a comparatively low cost.[67] In recent years, controlling of electrospun fibers assembled into desired micro- and/or nanostructures have received increasing attentions, for electrospun fibers with ordered microstructures and patterns may have specific

FIG. 8. Photograph of honeycomb. (Reprinted with permission from Kellex. Copyright 2011: Droid Life: A Droid Community Blog.) (Color figure available online.)

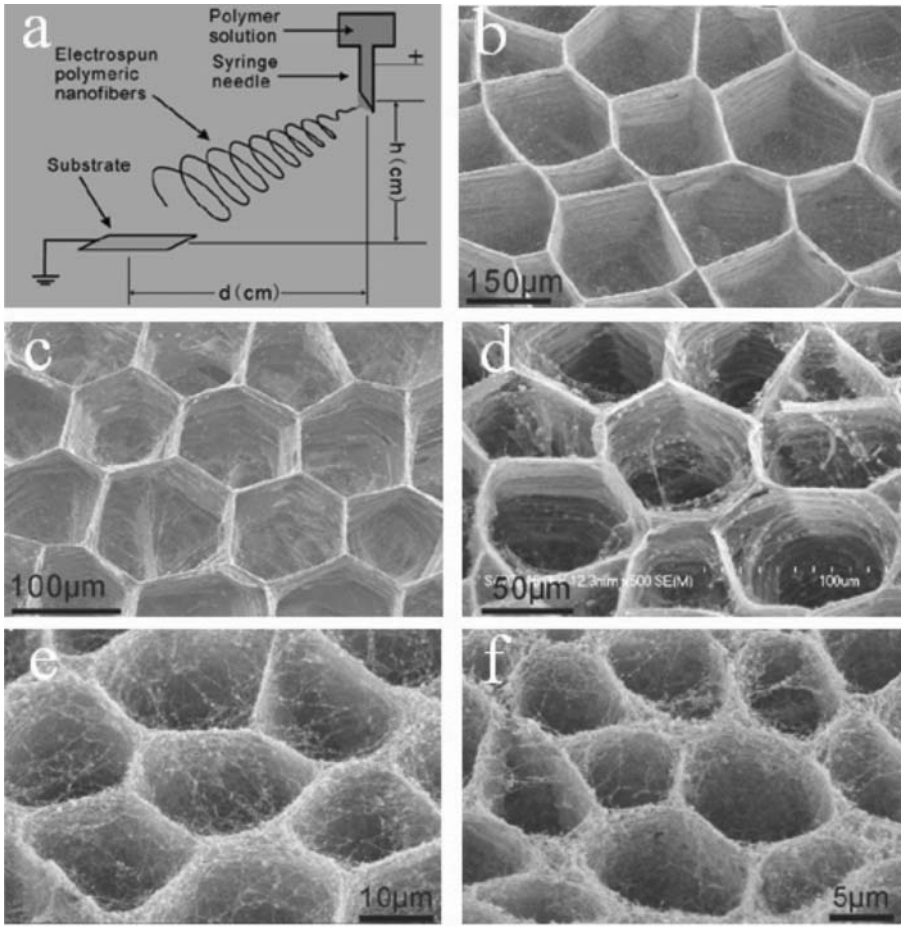

FIG. 9. (a) Schematic of the electrospinning setup. SEM images showing the surface morphology and wall structure of the honeycomb-patterned nanofibrous structures of PVA, PEO and PAN electrospun at different conditions: (b) PVA, concentration 6%, 22 kV, on plastic films; (c) PEO, concentration 3%, 22 kV, on Al substrates; (d) PEO, concentration 16%, 19 kV, on Al substrates; (d) PAN, concentration 16%, 19 kV, on Al substrates; (f) PAN, concentration 2%, 22 kV, on Al substrates. (Reprinted with permission from Yan et al.[68] Copyright 2011: American Chemical Society.)

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functions in numerous applications including microelectronic, photonic, and biomedical applications.[56]

Yan et al.[68] reported the fabrication of honeycomb-patterned nanofibrous structures through well-controlled self-assembly of continuous electrospun polymer nanofibers. They used electrospinning to produce charged polymer nanofibers, which were kept in the liquid state when landing on the substrates, by appropriately controlling the electrospinning conditions. Figure 9a shows the modified electrospinning setup for assembling electrospun fibers they utilized, and the substrates placed at an angular distance from needle nozzle is to avoid the droplet at a low concentration dripping on the fibrous mats damaging the samples. During electrospinning, these charged wet nanofibers were self-assembled into the honeycomb patterned nanofibrous structures driven by the competitive actions of surface tension and electrostatic repulsion. Several kinds of polymers (e.g., poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO) and polyacrylonitrile (PAN)) were electrospun into nanofibers and assembled into honeycomb-like structures as shown in Figures 9b to 9f, indicating that self-assembling electrospun nanofibers with honeycomb structures is a general phenomenon and applicable to many spinnable polymers.

4.4. Extracellular Matrix

Fortunately, the alignments of electrospun fibers have been extensively investigated by researchers,[53–55] which enables the fibrous mats composed of nanofibers with anisotropic property in two directions easily to be prepared. More interestingly, the composition of electrospun fibrous mats can be adjusted via blending polymer solutions,[69,70] adding additives into polymer solutions,[71] post-treatments,[72,73] as well as multi-jets

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spinning of different polymer solutions.[74,75] Therefore, not only the structures of electrospun fibrous mats can be controlled via electrospinning but also the composition of resultant fibers are adjustable, which makes the electrospinning technique as a good candidate for production of materials inspired from nature.

The natural extracellular matrices (ECM), which are composed of various protein fibrils and fibers interwoven within a hydrated network of glycosaminoglycan chains, mainly consist of three major types of biomolecules: (i) structural proteins, such as collagen and elastin, (ii) specialized proteins including fibrillin, fibronectin and laminin, and (iii) proteoglycans.[76] A lot of cells can organize their ECM with nanofibrous structural units which ranged from a few tens of nanometers to about a hundred of nanometers. The chemical compositions and biological aspects of such a hierarchically structured cellular environment affect the functions of cells and tissue profoundly, which can be mimicked by manipulating electrospun biodegradable and biocompatible polymer nanofibers with designed hierarchical structures and typical compositions.[77]

Over the past decade, a variety of natural (e.g., collagen, fibrinogen, elastin, etc.) and synthetic (e.g., poly(glycolic acid) (PGA), poly(lactic acid) (PLA), polycaprolactone (PCL), etc.) polymers have been electrospun into nanofibers in the form of nonwoven fibrous mats with three-dimensional (3D) hierarchical structures to mimic the ECM in bodies.[78] Researchers have demonstrated that the cells displayed a positive response to ECM made of electrospun collagen fibers. For instance, Matthews et al.[79,80] successfully prepared the various types of electrospun collagen fibers (e.g., I, II, and III) from HFP and found that the cells could propagate after seeding onto the resultant ECM. In addition to natural polymers, electrospun PGA, PLA, PCL and their copolymers fibrous mats also showed a good affinity to cells as good candidates for ECM to culture the cells. For example, Mo et al.[81] reported a biomimetic ECM comprising electrospun poly(L-lactide-co-ε-caprolactone) with L-lactide to ε-caprolactone ratio of 75 to 25 fibers for smooth muscle cells and endothelial cell proliferations, and the result indicated that the two kinds of cells adhered and proliferated well on the as-prepared ECM.

The bone system offers structures to the live body, protects internal organs and acts as a reservoir of calcium and phosphate. However, the fracture of bones and large bone defects owing to various traumas or natural ageing are typical types of tissue malfunction, which is still a challenge to regenerate for orthopaedic surgeons.[78,82] Fortunately, surface modification of electrospun fibers with ligands for specific cell receptors and ECM proteins, such as gelatin and calcium phosphate calcium phosphate layer, can improve their bioactivity in bone tissue engineering. In order to mimic the bone ECM and to provide a friendly interface with the host, Li et al.[72] fabricated the fibrous PCL scaffolds from via electrospinning, followed by a surface modification with gelatin via a layer-by-layer method and deposition of calcium phosphate using a mild mineralization procedure. Nandakumar et al.[83] developed a bone tissue engineering scaffold by coating the calcium phosphate onto electrospun fiber matrices. It is worth noting that the deposition of the calcium phosphate improved the *in vivo* bioactivity of the polymer. Alternatively, the biodegradable and biocompatible polymer solutions with inclusion of hydroxyapatite nanocrystals can also be electrospun into nanocompostie fibrous mats to mimic the human bone matrix, which exhibits good performances for bone regeneration.[71,84]

5. BIOMIMICRY VIA MANIPULATING INDIVIDUAL FIBER STRUCTURES

5.1. Lotus Leaf

Plant leaves exhibiting self-cleaning effects have received much more interests in recent years.[85] The lotus leaf is among the most well-known and studied examples, which exhibits well water-repellent properties (Figure 10a). The micromorphological characteristics of the lotus-leaf surfaces were also extensively studied, and it has been demonstrated that the lotus leaf surface is really rough due to the so-called papillose epidermal cells forming papillae or micro-level mound as shown in Figure 10b. Furthermore, the high-magnification SEM image of the papillae exhibits that its surface is also rough with nanoscale asperities comprising 3D epicuticular wax tubules (Figures 10c and 10d). The typical hierarchical structure of the surface enables the water droplets on the surface readily to sit on the apex of the micro- and/or nanostructures which trapped more air as a cushion under the droplets by displaying a superhydrophobicty with a WCA of about 160° (Figure 10e).[86]

Inspired by this fascinating phenomenon, researchers in the fields of science and industry have developed many methods, such as chemical deposition,[87] layer-by-layer deposition,[88] colloidal assembly,[89] and template-based techniques,[90] to yield artificial surfaces with the self-cleaning functionality. The fabrication of these artificial surfaces mainly depended on modifying a rough surface by chemical modification with low surface energy and making a rough surface from the low-surface-energy materials. In recent years, the electrospinning technique is widely used for producing superhydrophobic surfaces biomimicked from nature due to the morphology, structure, and properties of fibrous mats can be well and easily controlled by adjusting the spinning solution properties, the processing parameters as well as the ambient conditions.[64]

It is well known that electrospinning dilute polymer solutions can produce beads-on-string fibers or even polymer microspheres.[35] The shape and morphology of resultant beads can be also manipulated by changing the solvent compositions[91,92] In view of the versatility of electrospun fibrous mats, the artificial surfaces with characteristics of lotus leaves can be successfully produced via electrospinning. To mimic the topography of lotus leaves and to achieve a high WCA, Jiang et al.[93] fabricated the PS fibrous film via electrospinning dilute PS solution dissolved in *N,N*-dimethyl formamide (DMF). The resultant film is composed of porous microspheres (3 to 7 μm) and nanofibers

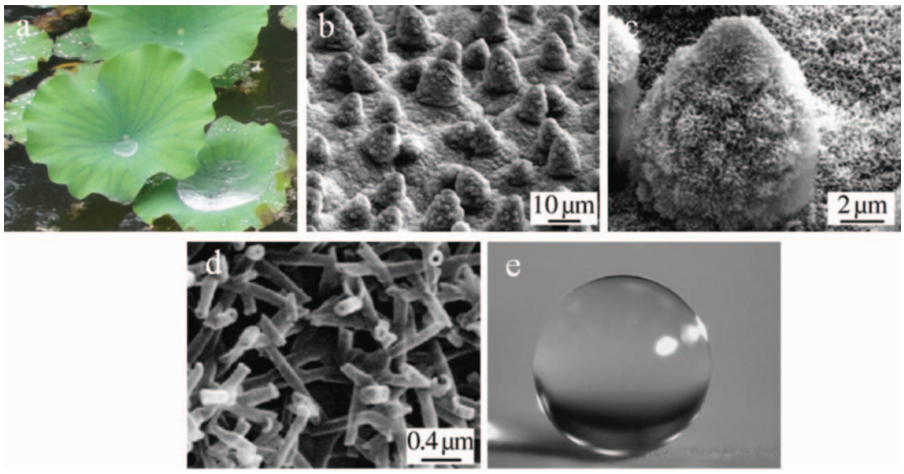

FIG. 10. (a) Photograph of lotus leaf in pool. SEM images (shown at three magnifications (b)–(d)) of lotus leaf surface, which consists of a microstructure formed by papillose epidermal cells covered with 3D epicuticular wax tubules on the surface which create nanostructure. (e) Image of a water droplet sitting on a lotus leaf. (Figures (b) to (e) reprinted with permission from Bhushan et al.[86] Copyright 2009: The Royal Society.) (Color figure available online.)

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(60 to 140 nm), which exhibits superhydrophobicity with a WCA greater than 160° as described in Figure 11. The porous microspheres of the resultant film play a leading role in the superhydrophobicity due to its hierarchical structure. Acatay et al.[94] also successfully fabricated a lotus-leaf-like structured fibrous mat with good superhydrophobicity by electrospinning a dilute polymer solution.

5.2. Silver Ragwort Leaf

The silver ragwort is another plant with hydrophobic leaves. Figure 12a shows the photograph of a silver ragwort. The plant leaves exhibit white-color which is not from any dye but related with the trichomes on the leaf surfaces.[95] The inset of Figure 12a displays the hydrophobicity of a silver ragwort leaf. The SEM images of the leaf surfaces present that the leaf is

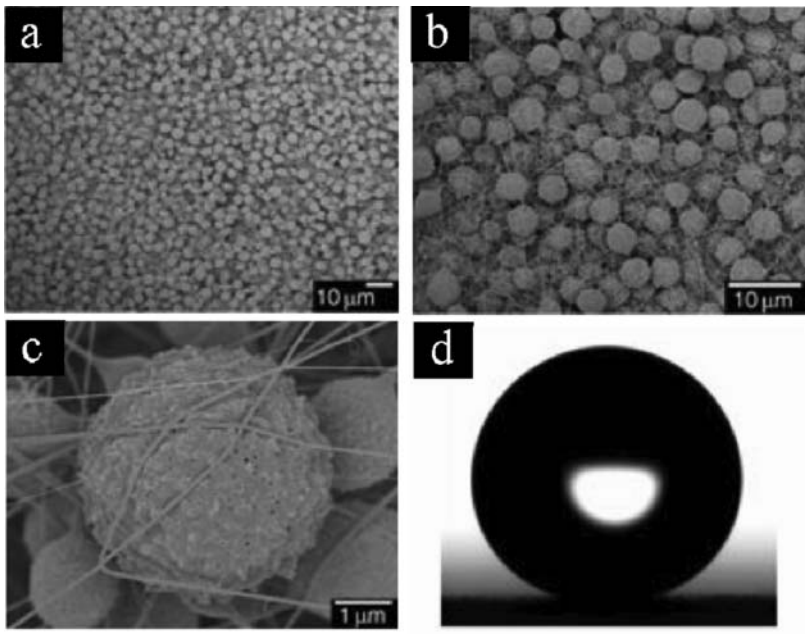

FIG. 11. (a) SEM image of porous microsphere/nanofiber composite film prepared from a 7 wt% PS/DMF solution. (b) Three dimensional network structure of the porous microsphere/nanofiber composite film. (c) Surface nanostructure of a single porous microsphere. (d) Water droplet on the resultant film. (Reprinted with permission from Jiang et al.[93] Copyright 2004: John Wiley & Sons, Inc.)

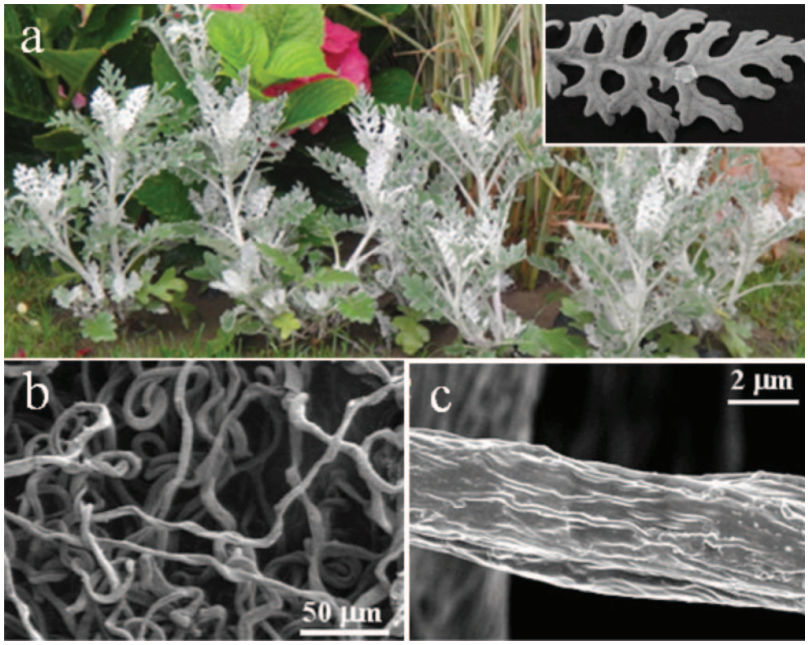

FIG. 12. (a) Photograph of the silver ragwort leaves. (b) and (c) SEM images of the leaf with different magnification. (Inset of Figure (a), Figures (b) and (c) reprinted with permission from Miyauchi et al.[39] Copyright 2006: IOP Publishing.) (Color figure available online.)

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covered by a lot of curved fibers with an average diameter about 5.6 μm (Figure 12b). Numerous grooves with diameters ranging from 100 to 200 nm are found along the fiber axis (Figure 12c). Measurements showed that the WCA on the leaf surface was about 147°.[31,94]

In order to prepare a functional surface imitating the silver ragwort, Ding et al.[39] prepared PS microfibers by electrospinning concentrate PS solutions and adjusted the fiber surface structures by changing the solvent compositions. Figure 13a shows SEM images of the electrospun PS fibers formed from solvent mixtures of tetrahydrofuran (THF) and DMF with weight ratio of 2/2. The fiber surfaces are covered with micrometre-sized oval pores along the fiber axis as shown in the inset of Figure 13a. At the THF/DMF weight ratio of 1/3, numerous short grooves (like elongated islands) with an average length of 1.43 μm and width of 158 nm along the fiber axis without the appearance of oval micropores are presented on the resultant fiber surfaces (Figure 13b). The typical surface morphology was explained by a rapid phase separation during the electrospinning process.[96] Measurements indicated that the resultant fiber surfaces exhibited a surperhydrophobicity with WCAs of 157.8° and 159.5°, respectively.

To improve the mechanical properties of the electrospun PS fibrous mats, Li et al.[75] modified the conventional electrospinning setup as shown in Figure 13c. The mechanical property of PS fibrous mats was significantly enhanced by adding the polyamide 6 (PA6) nanofibers homogenously into PS mats via a four-jet electrospinning process. Figures 13d and 13e show the SEM images of the blended fibrous mats of PS/PA6 with jets ratios of 1/3 and 2/2, respectively. The tensile test result indicated that the as-prepared blended fibrous mats at the critical jets ratio of 2/2 (PS/PA6) showed a three-times increased tensile strength compared with that of the pure PS fibrous mats. Meanwhile, the superhydrophobicity of the surface still held a WCA of 150°. Figure 13e shows several water droplets placed on the fibrous mats.[75]

Inspired by the lotus and silver ragwort leaves, Lin et al.[97] introduced a facile process to produce superhydrophobic mats with nano-protrusions and numerous grooves by one-step electrospinning of PS solutions incorporating various contents of silica nanoparticles as described in Figure 14. It was surprisingly noted that PS fibrous mats containing 14.3 wt% silica nanoparticles exhibited a stable superhydrophobic state with a WCA of 157.2° approaching that of the lotus leaf (160°).

5.3. Plant Tendril

Plant tendril is a long, tender, soft, curly, flexible and thread-like specialized stem. Once the tendril catches an object, it will curl into spirals or twist into a helix, often of one handedness over half of its length and of the opposite handedness over the other half, the two halves being connected by a short straight section, depending on whether they are supported at just one end or supported at both ends, respectively.[98] The circumnutation of plant tendril allows the plant to find support or attachment, which is of great use to the climbing plant.[98,99] Figure 15 displays the plant tendrils grow in nature forming helices and spirals.

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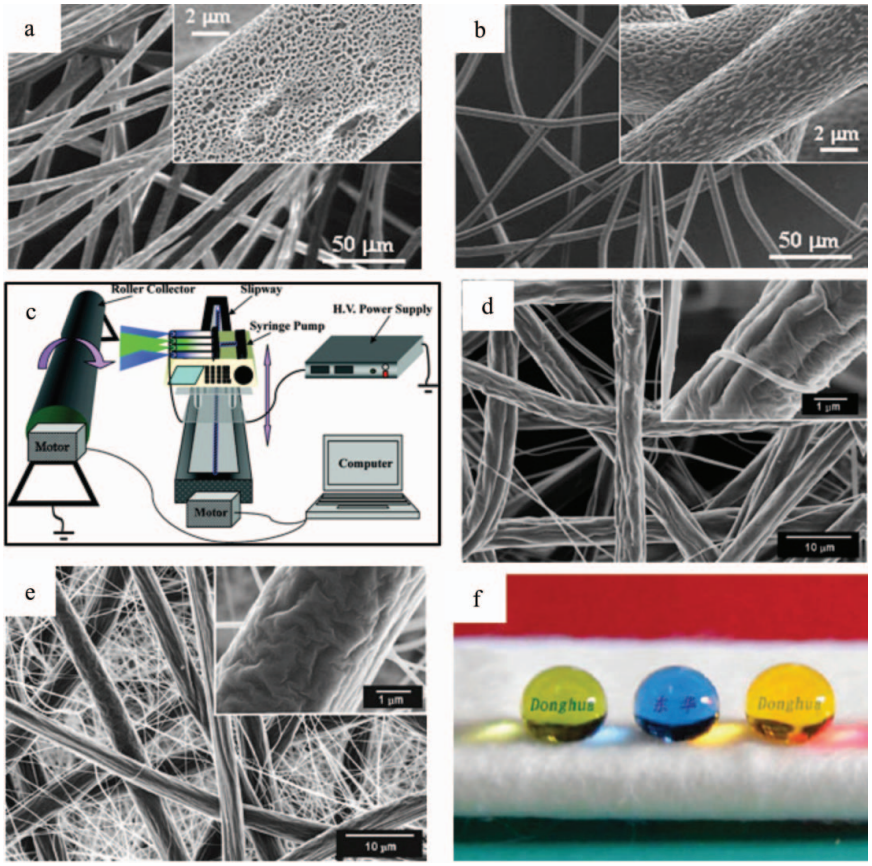

FIG. 13. SEM images of the electrospun PS fibers formed from various weight ratios of THF/DMF in solvent: (a) 2/2 and (b) 1/3. (c) Schematic of modified electrospinning setup for multi-jets electrospinning. SEM images of fibrous mats formed with various number ratios of jets of PS/PA6: (d) 3/1 and (e) 2/2. (f) Several water droplets placed on the fibrous mats formed with the number ratio of jets of 2/2 (PS/PA6) showing the superhydrophobicity. (Figures (a) and (b) reprinted with permission from Miyauchi et al.[39] Copyright 2006: IOP Publishing. Figures (c) to (f) reprinted with permission from Li et al.[75] Copyright 2009: American Chemical Society.) (Color figure available online.)

Inspired by the plant tendril, researchers found that the nanofibers with micro- and nanoscale helical structures exhibit some unique properties such as a much higher porosity, a good flexibility which enables them as good candidates for potential applications in areas comparing sensors, transducers, resonators, advanced optical components, and drug delivery systems.[100] To date, stable helices of porous manganese oxide materials have been produced from the contraction of a sol-gel upon solvent evaporation.[101] Nanoscale helical structures of zinc oxide and silicon dioxide were also generated by the vapor processing methods.[102,103]

More recently, electrospinning has been proved to an efficient and simple method to fabricate the helical nanofibers. For the electrospinning solution, two polymers with different properties such as different conductivities, and different elasticities are usually utilized. Figures 16a and 16b show the fluorescence microscopy images of poly(*p*-phenylene vinylene) (PPV)/polyvinyl pyrolidone (PVP) composite fibers that were prepared by electrospinning from PPV precursor/PVP in ethanol/DMF followed by thermal conversion at different spinning voltage. Additionally, the authors also investigated the factors affecting the formation of helices and provided a possible mechanism for its formation.[104] Kessick et al.[100] reported that microscale helical fibers could be electrospun from the nonconducting polymer PEO and the conducting polymer poly(aniline sulfonic acid). The results suggested that the helical microcoils were spontaneously produced on a conducting substrate due to the viscoelastic contraction of a linear fiber upon partial charge neutralization. Moreover, Shin et al.[105] reported the formation of pure helical nanofibers by electrospinning poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) dissolved in a mixture of water and ethyl alcohol (Figures 16c and 16d), which indicated that the helical fibers can also be generated from a single nonconducting polymer. This result demonstrated that the physical forces caused by the bending instability of the jet in electrospinning had a greater influence on the formation of helical structures than the effects of the electrical charge.[105] A similar phenomenon was also observed by Han et al.,[106] and the

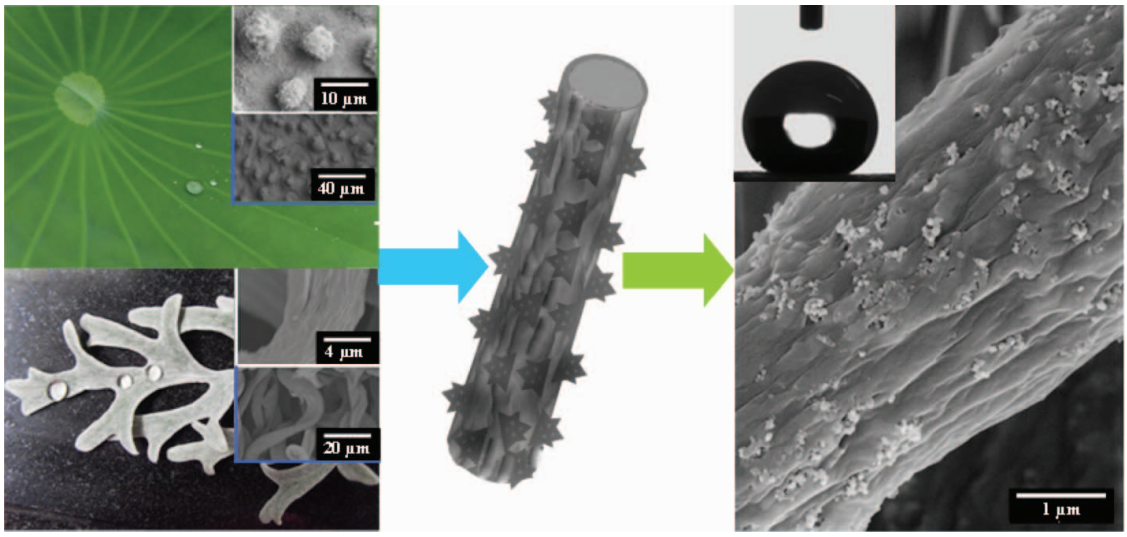

FIG. 14. Biomimetic superhydrophobic surfaces from a combination of the lotus leaf and silver ragwort leaf were fabricated via electrospinning PS solution with silica nanoparticles. (Reprinted by permission from Lin et al.[97] Copyright 2011: The Royal Society of Chemistry.) (Color figure available online.)

SEM images of resultant helical fibers were provided in Figures 16e and 16f.

The helical nanofibers resembling plant tendrils can also be easily produced by modifying the conventional electrospinning setup. For example, Lin et al.[107] developed a novel microfluidic electrospinning nozzle for co-electrospinning two polymer solutions side-by-side. Their investigation indicated that the side-by-side bi-component fiber can be bent to one side, forming crimped or helical fiber morphology, if the double-component sides have a differential shrinkage. By using this method, helical nanofibers have been successfully obtained when the fibers are electrospun from an elastomeric polymer, polyurethane, and a thermoplastic polymer, PAN.[107]

5.4. Soap-Bubble and Spider Web

It is well known that the morphology and diameter of electrospun fibers can be adjusted by tuning the solution properties, processing parameters as well as the ambient conditions.[9,28] In the past decade, great efforts have been made to decrease the diameter of electrospun fibers because the large average diameter of common electrospun fibers limits their further applications

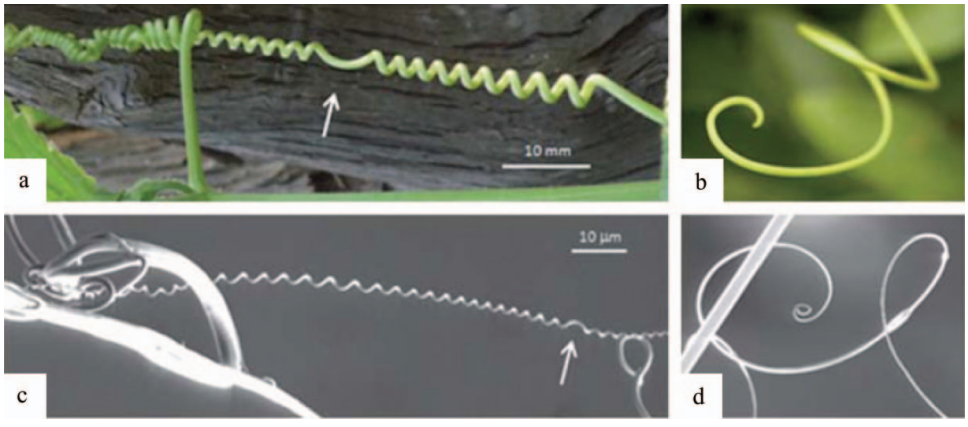

FIG. 15. (a) *Passiflora edulis* tendrils and cellulosic fibers form helices and spirals. Note the helix reversals–"perversions"–indicated by arrows in (a) and (c). Tendrils and fibers, if supported at both ends, twist into a helix of one handedness over half of its length and of the opposite handedness over the other half, the two halves being connected by a perversion. If supported at just one end, they curl into spirals (b) and (d). (Reprinted by permission from Godinho et al.[99] Copyright 2010: The Royal Society of Chemistry.) (Color figure available online.)

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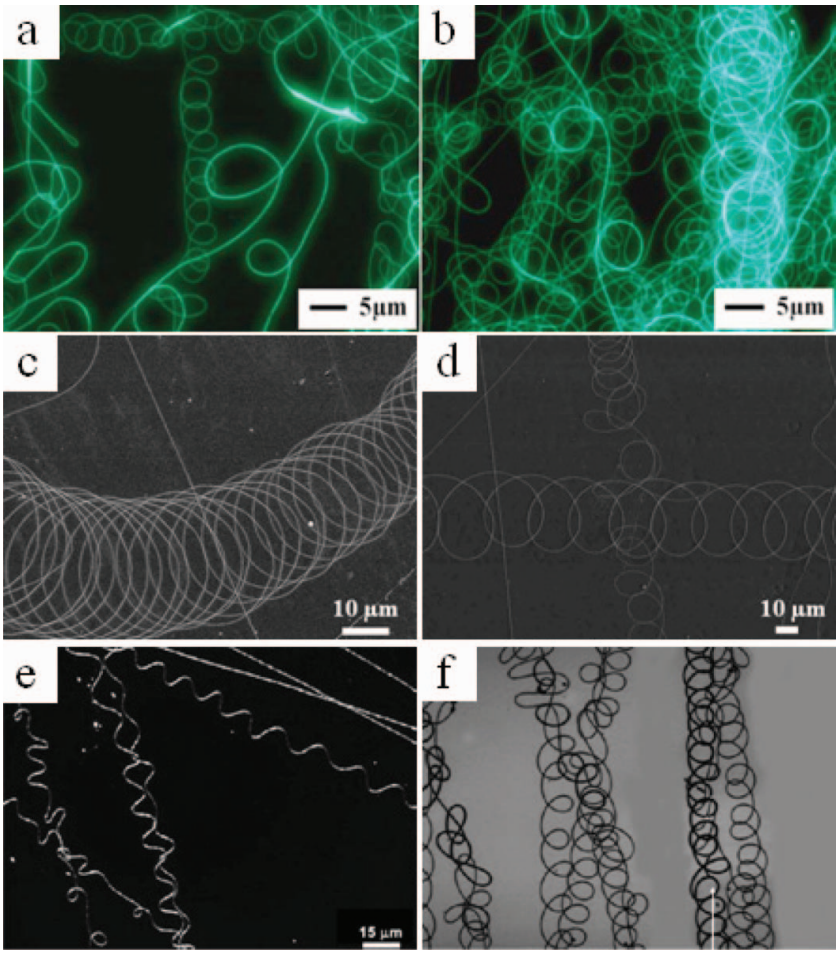

FIG. 16. Fluorescence microscopy images of PPV/PVP fibers that were prepared by electrospinning from PPV precursor/PVP in ethanol/DMF (a) under 7.5 kV and (b) 15 kV. SEM image showing (c) PAMPS helically structured nanofibers with regular-shaped coils and (d) crossed helical nanofibers deposited on an aluminum collector without the introduction of subelectrodes. (Reprinted with permission from Xin et al.[104] and Shin et al.[105] Copyright 2006: American Institute of Physics.) Optical micrographs of buckled bending electrospun (e) PEO fibers and (f) PA6 fibers. (Reprinted with permission from Han et al.[106] Copyright 2007: Elsevier.) (Color figure available online.)

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in ultra-filtration, ultra-sensitive sensors, catalysts, etc.[108] However, the objective of large-scale production of nanofibers with small diameter (<50 nm) via the conventional electrospinning was rarely achieved. In recent years, net-like structured membranes containing interlinked nanowires with a diameter less than 50 nm have been identified, which was first reported by Ding et al.[45] They obtained the PA6 and poly(acrylic acid) (PAA) nano-nets, and concluded that the nano-nets can be controlled by adjusting the solution properties and several parameters in the process of electrospinning.

Figure 17a shows the schematic diagrams illustrating the possible mechanism of nano-net formation during the electrospinning/netting process. The instability of the Taylor cone induced by the high electric field leads to the formation of the electrospray droplets.[109] During the flight of charged droplets from the capillary tip to the collector, the microsized droplet is distorted and expanded into a thin film due to the various forces such as the electrostatic force, the air resistance, the gravity, the Coulombic repulsion, the surface tension and the viscoelastic force (Figure 17b). The occurrence of rapid phase separation on the splitting-film and the minimal energy principle may result in the formation of such unexpected spider-web-like (Figure 17c) or soap-bubble-like (Figures 17d and 17e) nano-nets. A series of extensive studies indicated that the nano-nets were primitively regarded as a by-product caused by a high electric field that induces instability of suspended charged droplets during electrospinning rather than formed from the breaking jets.[110–113] Inspired from the spider web that can intercept

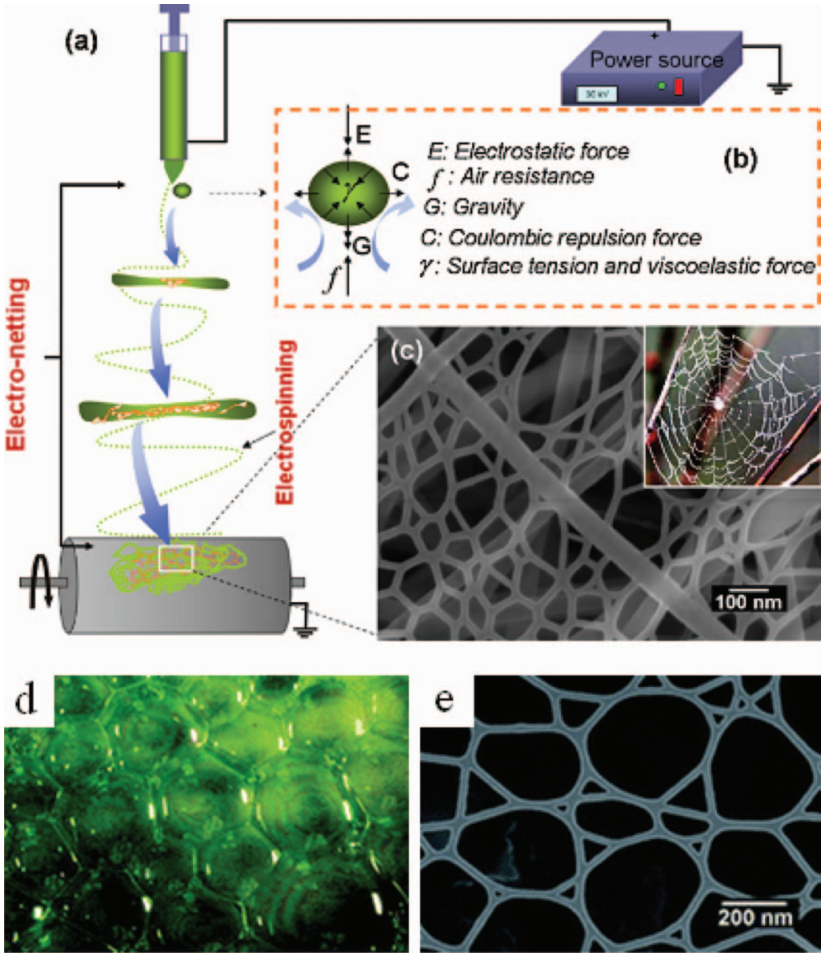

FIG. 17. Schematic diagrams illustrating the possible mechanism of nano-net formation during electrospinning/electro-netting process (a) and the forces acting on the charged droplet (b). (c) Typical FE-SEM image of gelatin/NaCl nano-nets. The inset is the optical image of spider-web. (Reprinted with permission from Wang et al.[113] Copyright 2011: Elsevier.) (d) Photograph of soap bubbles. (e) Soap-bubble-like structured PAA nano-nets. (Reprinted by permission from Yang et al.[111] Copyright 2011: The Royal Society of Chemistry.) (Color figure available online.)

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insects, spider-web-like nano-nets posses great potential for application as ultra-fine filters for the removal of particles or viruses with a size in the nanometre range.[112]

5.5. Polar Bear Hair

In the course of evolution over billions of years, animals, plants and insects in nature have developed more efficient solutions, such as self-cleaning, self-repair, energy conservation, thermal insulation, drag reduction, dry adhesion and so on, to adapt the living environment dealing with the challenges from the external world.[3] For example, feathers of many birds are hydrophobic due to their hierarchical structures (e.g., pigeon feather showing in Figure 6).[79] Further observation exhibits that many feathers are of multi-channel inner structure. These typical structures might reduce weight by decreasing friction with air and serve as heat-shields from intense solar radiation.[114] Multi-channel inner structures were also found in polar bear hair as shown in Figure 18, which contributed excellent thermal insulation and optical properties to the homeothermic species enabling them to survive in an extremely formidable polar environment.[115] These attractive features have inspired humans to achieve outstanding outcomes.

The 1D hollow nanomaterials such as carbon nanotubes have been extensively studied resulting in a broad range of important applications during the past two decades.[116] In recent ten years, electrospinning have been widely used to generate hollow nanofibers using two immiscible liquids through a coaxial, two-capillary spinneret, followed by selective removal of the cores. The circular cross-sections and well controlled orientation of hollow nanofibers prepared by this method make them particularly useful as nanofluidic channels as well as some other potential applications in catalysis, sensor, encapsulation, and drug delivery.[117,118]

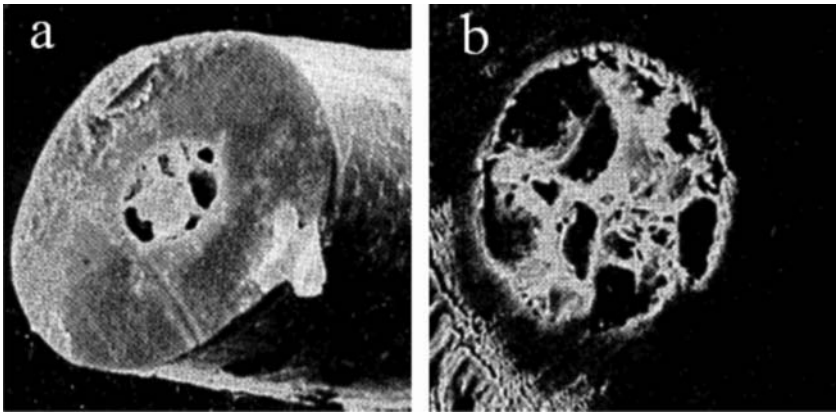

FIG. 18. (a) and (b) Scanning electron micrographs of polar bear hair-transverse sections with different magnification. (Reprinted with permission from Grojean et al.[115] Copyright 1980: Optical Society of America.)

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More recently, inspired by multi-channel inner structures of polar bear hair, Zhao et al.[119] developed a multi-fluidic compound-jet electrospinning technique to fabricate biomimetic hierarchical multi-channel microtubes. Figure 19a shows a schematic illustration of the experimental setup of the multi-fluidic compound-jet electrospinning, which is an example of three-channel tube fabrication system. It could be observed that the three metallic capillaries (as electrode to charge the fluids and delivering the inner fluid) were embedded in a spinneret (for outer fluid delivering) connected with syringe. They successfully prepared the TiO_2 three-channel microtubes by using a PVP/Ti(iOPr)$_4$ sol as the outer solution and paraffin as the inner fluidic system, followed by selective removal of the cores and the organic component. The SEM image of the cross section of resultant fibers is shown in Figure 19c. They have also demonstrated that the channel number of fibers could be tuned by changing the configuration of the compound nozzles. Figures 19b to 19e provide the SEM images of multi-channel tubes with variable diameters and channel numbers. The insets in each figure show the cross section illustrations of spinneret

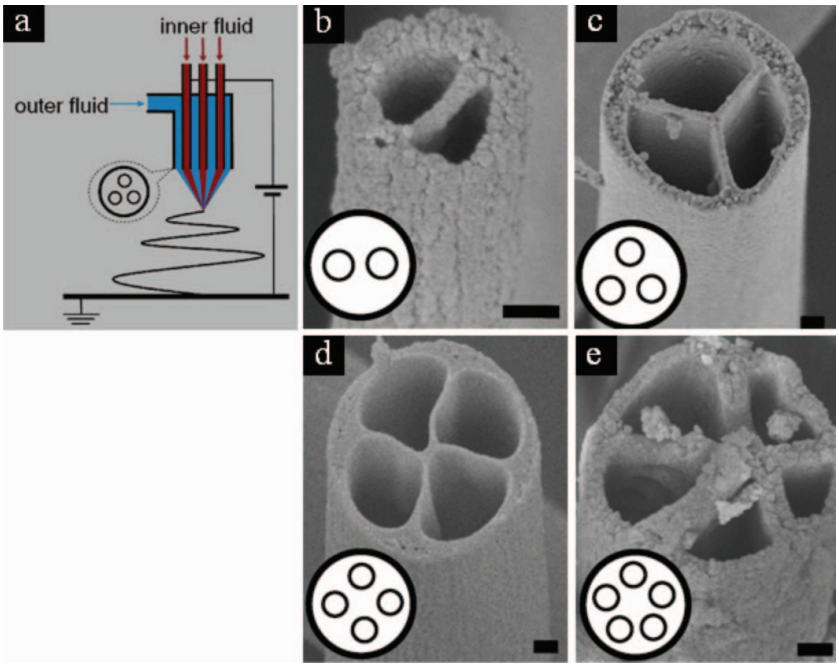

FIG. 19. (a) Schematic illustration of the three-channel tube fabrication system. (b-f) SEM images of multi-channel tubes with variable diameter and channel number. The inset in each figure shows the cross section illustration of spinneret that was used to fabricate the tube. The as-prepared tubes agree very well with the corresponding spinneret. Scale bars are 100 nm. (Reprinted with permission from Zhao et al.[119] Copyright 2007: American Chemical Society.) (Color figure available online.)

used to fabricate the tube which agree well with the corresponding fibers. Moreover, the composition, the wall thickness, and the tube diameters can be controlled by adjusting the experimental parameters. The method shows good feasibility and effectiveness for fabrication of multi-channel nanofibers with expectations.[119,120]

6. APPLICATIONS INSPIRED FROM NATURE

As discussed in the previous sections, electrospun fibers exhibit some unique properties, such as large surface-volume ratio, flexibility in surface functionalities, high porosity, high gas permeability, and small inter-fibrous pore size, which enable them as good candidates for a broad applications including tissue engineering, filtration, catalysis, self-cleaning, drug delivery system, sensors, DSSCs, etc.[10,28] Herein, some applications of the electrospun fibers only pertaining to biomimicked from nature are briefly discussed as follows.

6.1. Self-Cleaning Materials

Superhydrophobic surfaces are very important for contamination prevention. Water repellency exhibits self-cleaning functions due to the contaminants easily removed as water rolls off on surfaces.[42] Based on the fundamental principles of fabricating superhydrophobic surfaces,[121] the self-cleaning materials biomimicked from nature such as lotus leaf, silver ragwort leaf, and feathers can be efficiently generated via electrospinning techniques including mainly two routes, i.e., electrospinning the polymers with low surface energy (hydrophobic materials) into hierarchical architectures,[39,64,93,94,97] and modifying the electrospun fiber mats with low surface energy materials.[122,123]

6.2. Tissue Engineering

Tissues are the platforms for regeneration comprising cartilage, bone, skin tissue, blood vessels, and so on. The suitable tissue engineering needs prepared scaffolds owning similar chemical compositions, morphologies, and surface functional groups as the natural counterparts.[60,79] Fortunately, electrospinning technique provides good opportunities to mimic the natural ECM for tissue growth composed of a 3D fiber network made of various proteins with hierarchical structures from nanoscales to macroscales, which has been well discussed in the previous sections. Some published papers have thoroughly reviewed the applications of electrospun nanofibers in varios tissues as EMC.[10,82]

6.3. Sensors

Electrospun fibers, offering a high surface-volume ratio, are applicable for sensitive and fast sensing as sensor materials. For example, Ding et al.[124] successfully fabricated a novel gas sensor by coating PAA and PVA nanofibrous membrane with fiber diameter 100 to 400 nm onto quartz crystal microbalance (QCM) by electrospinning to detect NH_3. The result indicated that nanofibrous membranes coated QCM showed much higher gas sensitivity than that of continuous film with the same compositions coated QCM. The sensors based on electrospun fibrous membrane have been well developed, which was thoroughly reviewed by Ding et al.[8] More interestingly, spider-web-like nanonets containing interlinked nanowires with ultra-thin diameter less than 50 nm have been identified via electro-netting process, whose diameter is about one order of magnitude less than that of conventional electrospun fibers.[125] Wang et al.[110,112] fabricated the sensors based upon QCM using nano-nets as novel sensitive materials to detect the humidity and the trimethylamine. The results showed that the performance of the resultant sensors can be greatly upgraded due to the smaller fiber diameters of nano-nets.

6.4. Catalysis and Others

In the preceding sections, we have discussed some inorganic nanofibers with novel structures biomimicked from nature by electrospinning combined with calcinations. The hollow fibers with tunable inner structures provide much higher specific surface area compared with the solid fibers, which enable them suitable for applications in catalysis. For example, Zhan et al.[118] used the long TiO_2 hollow fibers with mesoporous walls prepared by the sol-gel two-capillary spinneret electrospinning technique to decompose the methylene blue and gaseous formaldehyde. The results showed that the as-prepared TiO_2 fibers had higher photocatalytic activities than the commercial TiO_2 nanoparticles and the corresponding mesoporous TiO_2 powders. Zhao et al.[126] utilized the polar bear hair-inspired multi-channel TiO_2 fibers as catalysis to degrade the gaseous acetaldehyde. The results showed that the channel structure increased the surface areas by 0.79%, 21.4%, and 94.2% from 1 channel, 2 channels, to 3 channels, respectively, compared with zero-channel, and the 3 channels TiO_2 fibers exhibited the highest photocatalytic activity.[126] Furthermore, the long hollow fibers can be conveniently fixed and reclaimed as good candidates for photocatalytic applications.

Additionally, we believed that the spider-web-like nano-nets may be available for ultra-filtration to intercept viruses and bacteria such as influenza A (H1N1) virus, severe acute respiratory syndrome (SARS) virus, and Escherichia coli due to their smaller fiber diameters.[8]

7. SUMMARY

Electrospinning has been experienced nearly one hundred years since it became an available technique to generate ultra-thin polymer fibers with diameters ranging from several nanometers to a few micrometers. During the past two decades, electrospinning has aroused increasingly interests both in academic research and practical applications. In this critical review, we introduced the origin of electrospinning briefly and reviewed its development track in detail, and then we described the basic setup of electrospinning and discussed the manipulation of

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resultant fiber morphology via tuning the parameters during electrospinning.

The straightforward and easy manipulation of electrospun fibers such as their assemblies (e.g., random or aligned with design), individual fiber morphology (e.g., beaded-fiber, bead-free fiber, porous, core-sheath and hollow), and chemical compositions enables this technique as an efficient way to create materials with micro- and/or nanostructures existing in nature, referring to "biomimetics". As shown in recent demonstrations, the spinning process such as the spider silk can be imitated via electrospinning with some modifications. Because of the well tunable morphology, structures and compositions of the electrospun fibers, a number of fascinating structures of objects in nature, including some plant leaves, feathers, honeycomb, ECM, plant tendril, soap-bubble and spider webs, polar bear hair and so on, have been successfully biomimicked via electrospinning, sometimes, with subsequent post-treatments.

The nanomaterials bio-inspired from nature via electrospinning showed some advantages or excellent performances in the applications of self-cleaning materials, tissue engineering, sensors, catalysts, etc. These superiorities include that the self-cleaning materials can be obtained via electrospinning directly or with some post-treatment, easily formation of ECM with the same compositions as well as architectures of native ECM for tissue engineering, upgrading the performance of sensors due to the much smaller diameters of nano-nets, increasing the photocatalytic activities of electrospun fibers used as a catalyst. We are expecting this review to be a bright guiding lamp for researchers to develop more and more bio-inspired nanomaterials with new functionalities.

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ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (No. 50803009 and 51173022), the "111 Project" (No. 111-2-04 and B07024), the Shanghai Committee of Science and Technology (No. 10JC1400600), the National Basic Research Program of China (973 Program, 2011CB606103), the Innovation Program of Shanghai Municipal Education Commission (11ZZ59), and the "Dawn" Program of Shanghai Education Commission (10SG32).

REFERENCES

1. M. A. Meyers, P. Y. Chen, A. Y. M. Lin, and Y. Seki, Biological materials: Structure and mechanical properties, *Prog. Mater Sci.*, **53**, 1 (2008).
2. K. Liu, X. Yao, and L. Jiang, Recent developments in bio-inspired special wettability, *Chem. Soc. Rev.*, **39**, 3240 (2010).
3. L. Eadie and T. K. Ghosh, Biomimicry in textiles: past, present and potential. An over review, *J. R. Soc. Interface.*, **8**, 761 (2011).
4. A. K. Pahl, A. Bowyer, N. R. Bogatyrev, O. A. Bogatyreva, and J. F. V. Vincent, Biomimetics: its practice and theory, *J. R. Soc. Interface.*, **3**, 471 (2006).
5. O. H. Schmitt, in *Proc. 3rd Int. Biophysics Congress*, Boston, p. 297 (1969).
6. B. Bhushan and Y. C. Jung, Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction, *Prog. Mater Sci.*, **56**, 1 (2011).
7. B. Bhushan, Biomimetics: lessons from nature-an overview, *Phil.Trans. R. Soc. A*, **367**, 1445 (2009).
8. B. Ding, M. R. Wang, X. F. Wang, J. Y. Yu, and G. Sun, Electrospun nanomaterials for ultrasensitive sensors, *Mater. Today*, **13**, 16 (2010).
9. D. Li and Y. N. Xia, Electrospinning of nanofibers: Reinventing the wheel? *Adv. Mater.*, **16**, 1151 (2004).
10. A. Greiner and J. H. Wendorff, Electrospinning: A fascinating method for the preparation of ultrathin fibres, *Angew. Chem. Int. Edit.*, **46**, 5670 (2007).
11. W. J. Morton, Method of dispersing fluids, *U.S. Patent No.705691* (1902).
12. J. F. Cooley, Apparatus for electrically dispersing fluids, *U.S. Patent No. 692631* (1902).
13. J. F. Cooley, Electrical method of dispersing fluids, *U.S. Patent No. 745276* (1903).
14. J. Zeleny, The electrical discharge from liquid points, and a hydrostatic method of measuring the electric intensity at their surfaces, *Phys. Rev.*, **3**, 69 (1914).
15. J. Zeleny, Instability of electrified liquid surfaces, *Phys. Rev.*, **10**, 1 (1917).
16. A. Formhals, Process and apparatus for preparing artificial threads, *U.S. Patent No. 1975504* (1934).
17. Method of and apparatus for producing fibrous or filamentary material, *U.S. Patent No. 2048651* (1936).
18. M. A. Formhals, Method and apperatus for the production of fibers, *U.S. Patent No. 2123992* (1938).
19. P. A. Formhals, Production of artifical fibers from fiber forming liquids, *U.S. Patent No. 2323025* (1943).
20. D. G. Taylor, Disintegration of water drops in an electric field, *Proc. R. Soc. Lond. A*, **280**, 383 (1964).
21. E. G. Taylor, Electrically driven jets, *Proc. R. Soc. Lond. A*, **313**, 453 (1969).
22. P. K. Baumgarten, Electrostatic spinning of acrylic microfibers, *J. Colloid Interface Sci.*, **36**, 71 (1971).
23. L. Larrando and R. S. Manley, Electrostatic fiber spinning from polymer melts. I. Experimental observations on fiber formation and properties, *J Polym Sci: Polym Phys Ed*, **19**, 909 (1981).
24. E. L. Larrondo and R. St John Manley, Electrostatic fiber spinning from polymer melts. II. Examination of the flow field in an electrically driven jet, *J Polym Sci: Polym Phys Ed*, **19**, 921 (1981).
25. J. Doshi and D. H. Reneker, Electrospinning process and applications of electrospun fibers, *J. Electrostatics*, **35**, 151 (1995).
26. D. H. Reneker and I. Chun, Nanometre diameter fibres of polymer, produced by electrospinning, *Nanotechnology*, **7**, 216 (1996).
27. B. Ding and J. Y. Yu, Electrospinning and nanofibers, *China Textile & Apparel Press*, 11 (2011).
28. Z. M. Huang, Y. Z. Zhang, M. Kotaki, and S. Ramakrishna, A review on polymer nanofibers by electrospinning and their applications in nanocomposites, *Compos. Sci. Technol.*, **63**, 2223 (2003).
29. A. F. Spivak, Y. A. Dzenis, and D. H. Reneker, A model of steady state jet in the electrospinning process, *MeReC*, **27**, 37 (2000).

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30. M. M. Hohman, M. Shin, G. Rutledge, and M. P. Brenner, Electrospinning and electrically forced jets. I. Stability theory, *Phys. Fluids*, **13**, 2201 (2001).
31. A. L. Yarin, S. Koombhongse, and D. H. Reneker, Bending instability in electrospinning of nanofibers, *J. Appl. Phys.*, **89**, 3018 (2001).
32. V. Y. Shkadov and A. A. Shutov, Disintegration of a charged viscous jet in a high electric field, *Fluid Dyn. Res.*, **28**, 23 (2001).
33. M. McKee, J. Layman, M. Cashion, and T. Long, Phospholipid nonwoven electrospun membranes, *Science*, **311**, 353 (2006).
34. J. Y. Lin, B. Ding, J. Y. Yu, and Y. Hsieh, Direct fabrication of highly nanoporous polystyrene fibers via electrospinning, *ACS Appl. Mater. Interfaces.*, **2**, 521 (2010).
35. H. Fong, I. Chun, and D. H. Reneker, Beaded nanofibers formed during electrospinning, *Polymer*, **40**, 4585 (1999).
36. M. M. Munir, A. B. Suryamas, F. Iskandar, and K. Okuyama, Scaling law on particle-to-fiber formation during electrospinning, *Polymer*, **50**, 4935 (2009).
37. C. Zhang, X. Yuan, L. Wu, Y. Han, and J. Sheng, Study on morphology of electrospun poly (vinyl alcohol) mats, *Eur. Polym. J.*, **41**, 423 (2005).
38. M. Bognitzki, W. Czado, T. Frese, A. Schaper, M. Hellwig, M. Steinhart, A. Greiner, and J. H. Wendorff, Nanostructured fibers via electrospinning, *Adv. Mater.*, **13**, 70 (2001).
39. Y. Miyauchi, B. Ding, and S. Shiratori, Fabrication of a silver-ragwort-leaf-like super-hydrophobic micro/nanoporous fibrous mat surface by electrospinning, *Nanotechnology*, **17**, 5151 (2006).
40. J. M. Deitzel, J. Kleinmeyer, D. Harris, and N. C. B. Tan, The effect of processing variables on the morphology of electrospun nanofibers and textiles, *Polymer*, **42**, 261 (2001).
41. Y. Shin, M. Hohman, M. Brenner, and G. Rutledge, Experimental characterization of electrospinning: the electrically forced jet and instabilities, *Polymer*, **42**, 09955 (2001).
42. C. J. Buchkoa, L. C. Chena, Y. Shena, and D. C. Martina, Processing and microstructural characterization of porous biocompatible protein polymer thin films, *Polymer*, **40**, 7397 (1999).
43. S. R. Givens, K. H. Gardner, J. F. Rabolt, and D. B. Chase, High-temperature electrospinning of polyethylene microfibers from solution, *Macromolecules*, **40**, 608 (2007).
44. J. Li, A. He, J. Zheng, and C. C. Han, Gelatin and gelatin–hyaluronic acid nanofibrous membranes produced by electrospinning of their aqueous solutions, *Biomacromolecules*, **7**, 2243 (2006).
45. B. Ding, C. R. Li, Y. Miyauchi, O. Kuwaki, and S. Shiratori, Formation of novel 2D polymer nanowebs via electrospinning, *Nanotechnology*, **17**, 3685 (2006).
46. S. Tripatanasuwan, Z. X. Zhong, and D. H. Reneker, Effect of evaporation and solidification of the charged jet in electrospinning of poly(ethylene oxide) aqueous solution, *Polymer*, **48**, 5742 (2007).
47. C. L. Casper, J. S. Stephens, N. G. Tassi, D. B. Chase, and J. F. Rabolt, Controlling surface morphology of electrospun polystyrene fibers: effect of humidity and molecular weight in the electrospinning process, *Macromolecules*, **37**, 573 (2004).
48. C. L. Pai, M. C. Boyce, and G. C. Rutledge, Morphology of porous and wrinkled fibers of polystyrene electrospun from dimethylformamide, *Macromolecules*, **42**, 2102 (2009).
49. F. Vollrath and D. P. Knight, Liquid crystalline spinning of spider silk, *Nature*, **410**, 541 (2001).
50. H. J. Jin and D. L. Kaplan, Mechanism of silk processing in insects and spiders, *Nature*, **424**, 1057 (2003).
51. J. H. He, Y. Liu, L. Xu, J. Y. Yu, and G. Sun, Biomimic fabrication of electrospun nanofibers with high-throughput, *Chaos Solitons Fractals*, **37**, 643 (2008).
52. D. P. Knight and F. Vollrath, Spinning an elastic ribbon of spider silk, *Philos. Trans. R. Soc. Lond. B. Biol. Sci.*, **357**, 219 (2002).
53. G. Mathew, J. P. Hong, J. M. Rhee, D. J. Leo, and C. Nah, Preparation and anisotropic mechanical behavior of highly-oriented electrospun poly(butylene terephthalate) fibers, *J. Appl. Polym. Sci.*, **101**, 2017 (2006).
54. A. Theron, E. Zussman, and A. L. Yarin, Electrostatic field-assisted alignment of electrospun nanofibres, *Nanotechnology*, **12**, 384 (2001).
55. D. Li, Y. L. Wang, and Y. N. Xia, Electrospinning of polymeric and ceramic nanofibers as uniaxially aligned arrays, *Nano Lett.*, **3**, 1167 (2003).
56. D. M. Zhang and J. Chang, Patterning of electrospun fibers using electroconductive templates, *Adv. Mater.*, **19**, 3664 (2007).
57. J. M. Deitzel, J. D. Kleinmeyer, J. K. Hirvonen, and N. C. B. Tan, Controlled deposition of electrospun poly(ethylene oxide) fibers, *Polymer*, **42**, 8163 (2001).
58. D. Yang, B. Lu, Y. Zhao, and X. Jiang, Fabrication of aligned fibrous arrays by magnetic electrospinning, *Adv. Mater.*, **19**, 3702 (2007).
59. L. Feng, S. H. Li, Y. S. Li, H. J. Li, L. J. Zhang, J. Zhai, Y. L. Song, B. Q. Liu, L. Jiang, and D. B. Zhu, Super-hydrophobic surfaces: From natural to artificial, *Adv. Mater.*, **14**, 1857 (2002).
60. J. Zhang, J. Wang, Y. Zhao, L. Xu, X. Gao, Y. Zheng, and L. Jiang, How does the leaf margin make the lotus surface dry as the lotus leaf floats on water?, *Soft Matter*, **4**, 2232 (2008).
61. H. Wu, R. Zhang, Y. Sun, D. Lin, Z. Sun, W. Pan, and P. Downs, Biomimetic nanofiber patterns with controlled wettability, *Soft Matter*, **4**, 2429 (2008).
62. E. Bormashenko, Y. Bormashenko, T. Stein, G. Whyman, and E. Bormashenko, Why do pigeon feathers repel water? Hydrophobicity of pennae, Cassie–Baxter wetting hypothesis and Cassie–Wenzel capillarity-induced wetting transition, *J. Colloid Interface Sci.*, **311**, 212 (2007).
63. A. Tuteja, W. Choi, J. M. Mabry, G. H. McKinley, and R. E. Cohen, Robust omniphobic surfaces, *PNAS*, **105**, 18200 (2008).
64. M. Ma, R. M. Hill, and G. C. Rutledge, A review of recent results on superhydrophobic materials based on micro- and nanofibers, *J. Adhes. Sci. Technol.*, **22**, 1799 (2008).
65. W. J. Roberts, Honeycomb geometry: Applied mathematics in nature, *Mathematics Teacher*, **77**, 188 (1984).
66. D. Mackenzie, Proving the perfection of the honeycomb, *Science*, **285**, 1338 (1999).
67. G. Widawski, M. Rawiso, and B. Francois, Self-organized honeycomb morphology of star-polymer polystyrene films, *Nature*, **369**, 387 (1994).
68. G. Yan, J. Yu, Y. Qiu, X. Yi, J. Lu, X. Zhou, and X. Bai, Self-assembly of electrospun polymer nanofibers: a general phenomenon generating honeycomb-patterned nanofibrous structures, *Langmuir*, **27**, 4285 (2011).

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69. J. Du and Y. L. Hsieh, Cellulose/chitosan hybrid nanofibers from electrospinning of their ester derivatives, *Cellulose*, **16**, 247 (2009).
70. K. E. Park, H. K. Kang, S. J. Lee, B. M. Min, and W. H. Park, Biomimetic nanofibrous scaffolds: Preparation and characterization of PGA/chitin blend nanofibers, *Biomacromolecules*, **7**, 635 (2006).
71. G. M. Kim, P. Simon, and J. S. Kim, Electrospun PVA/HAp nanocomposite nanofibers: biomimetics of mineralized hard tissues at a lower level of complexity, *Bioinspir. Biomim.*, **3**, 46003 (2008).
72. X. R. Li, J. W. Xie, X. Y. Yuan, and Y. N. Xia, Coating electrospun poly(epsilon-caprolactone) fibers with gelatin and calcium phosphate and their use as biomimetic scaffolds for bone tissue engineering, *Langmuir*, **24**, 14145 (2008).
73. F. Yang, J. G. C. Wolke, and J. A. Jansen, Biomimetic calcium phosphate coating on electrospun poly (epsilon-caprolactone) scaffolds for bone tissue engineering, *Chem. Eng. J.*, **137**, 154 (2008).
74. B. Ding, E. Kimura, T. Sato, S. Fujita, and S. Shiratori, Fabrication of blend biodegradable nanofibrous nonwoven mats via multi-jet electrospinning, *Polymer*, **45**, 1895 (2004).
75. X. H. Li, B. Ding, J. Y. Lin, J. Y. Yu, and G. Sun, Enhanced mechanical properties of superhydrophobic microfibrous polystyrene mats via polyamide 6 nanofibers, *J. Phys. Chem. C*, **113**, 20452 (2009).
76. M. P. Lutolf and J. A. Hubbell, Synthetic biomaterials as instructive extracellular microenvironments for morphogenesis in tissue engineering, *Nat. Biotechnol.*, **23**, 47 (2005).
77. D. H. Kim, H. Lee, Y. K. Lee, J. M. Nam, and A. Levchenko, Biomimetic nanopatterns as enabling tools for analysis and control of live cells, *Adv. Mater.*, **22**, 4551 (2010).
78. S. Sell, C. Barnes, M. Smith, M. McClure, P. Madurantakam, J. Grant, M. McManus, and G. Bowlin, Extracellular matrix regenerated: tissue engineering via electrospun biomimetic nanofibers, *Polym. Int.*, **56**, 1349 (2007).
79. J. A. Matthews, G. E. Wnek, D. G. Simpson, and G. L. Bowlin, Electrospinning of collagen nanofibers, *Biomacromolecules*, **3**, 232 (2002).
80. J. A. Matthews, E. D. Boland, G. E. Wnek, D. G. Simpson, and G. L. Bowlin, Electrospinning of collagen type II: A feasibility study, *J. Bioact. Compatible Polym.*, **18**, 125 (2003).
81. X. M. Mo, C. Y. Xu, M. Kotaki, and S. Ramakrishna, Electrospun P(LLA-CL) nanofiber: a biomimetic extracellular matrix for smooth muscle cell and endothelial cell proliferation, *Biomaterials*, **25**, 1883 (2004).
82. J. Venugopal, M. P. Prabhakaran, Y. Zhang, S. Low, A. T. Choon, and S. Ramakrishna, Biomimetic hydroxyapatite-containing composite nanofibrous substrates for bone tissue engineering, *Phil. Trans. R. Soc. A*, **368**, 2065 (2010).
83. A. Nandakumar, L. Yang, P. Habibovic, and C. van Blitterswijk, Calcium phosphate coated electrospun fiber matrices as scaffolds for bone tissue engineering, *Langmuir*, **26**, 7380 (2010).
84. H. W. Kim, J. H. Song, and H. E. Kim, Nanofiber generation of gelatin–hydroxyapatite biomimetics for guided tissue regeneration, *Adv. Funct. Mater.*, **15**, 1988 (2005).
85. K. Koch, B. Bhushan, and W. Barthlott, Multifunctional surface structures of plants: An inspiration for biomimetics, *Prog. Mater Sci.*, **54**, 137 (2009).
86. B. Bhushan, Y. C. Jung, and K. Koch, Micro-, nano- and hierarchical structures for superhydrophobicity, self-cleaning and low adhesion, *Phil. Trans. R. Soc. A*, **367**, 1631 (2009).
87. X. F. Wu and G. Q. Shi, Production and characterization of stable superhydrophobic surfaces based on copper hydroxide nanoneedles mimicking the legs of water striders, *J. Phys. Chem. B*, **110**, 11247 (2006).
88. T. Ogawa, B. Ding, Y. Sone, and S. Shiratori, Super-hydrophobic surfaces of layer-by-layer structured film-coated electrospun nanofibrous membranes, *Nanotechnology*, **18**, 165607 (2007).
89. G. Zhang, D. Y. Wang, Z. Z. Gu, and H. Mohwald, Fabrication of superhydrophobic surfaces from binary colloidal assembly, *Langmuir*, **21**, 9143 (2005).
90. H. Yan, K. Kurogi, H. Mayama, and K. Tsujii, Environmentally stable super water-repellent poly(alkylpyrrole) films, *Angew. Chem. Int. Edit.*, **44**, 3453 (2005).
91. J. Liu and S. Kumar, Microscopic polymer cups by electrospinning, *Polymer*, **46**, 3211 (2005).
92. J. Liu, A. Rasheed, H. M. Dong, W. W. Carr, M. D. Dadmun, and S. Kumar, Electrospun micro- and nanostructured polymer particles, *Macromol. Chem. Phys.*, **209**, 2390 (2008).
93. L. Jiang, Y. Zhao, and J. Zhai, A lotus-leaf-like superhydrophobic surface: A porous microsphere/nanofiber composite film prepared by electrohydrodynamics, *Angew. Chem. Int. Edit.*, **43**, 4338 (2004).
94. K. Acatay, E. Simsek, C. Ow-Yang, and Y. Z. Menceloglu, Tunable, superhydrophobically stable polymeric surfaces by electrospinning, *Angew. Chem. Int. Edit.*, **43**, 5210 (2004).
95. Z. Z. Gu, H. M. Wei, R. Q. Zhang, G. Z. Han, C. Pan, H. Zhang, X. J. Tian, and Z. M. Chen, Artificial silver ragwort surface, *Appl. Phys. Lett.*, **86**, 201915 (2005).
96. S. Megelski, J. S. Stephens, D. B. Chase, and J. F. Rabolt, Micro- and nanostructured surface morphology on electrospun polymer fibers, *Macromolecules*, **35**, 8456 (2002).
97. J. Y. Lin, Y. Cai, X. F. Wang, B. Ding, J. Y. Yu, and M. R. Wang, Fabrication of biomimetic superhydrophobic surfaces inspired by lotus leaf and silver ragwort leaf, *Nanoscale*, **3**, 1258 (2011).
98. N. S. Liou and G. W. Ruan, The mechanical properties of tendril of climbing plant, *Mechanics of Biological Systems and Materials*, **2**, 101 (2011).
99. M. H. Godinho, J. P. Canejo, G. Feio, and E. M. Terentjev, Self-winding of helices in plant tendrils and cellulose liquid crystal fibers, *Soft Matter*, **6**, 5965 (2010).
100. R. Kessick and G. Tepper, Microscale polymeric helical structures produced by electrospinning, *Appl. Phys. Lett.*, **84**, 4807 (2004).
101. I. Veretennikov, A. Indeikina, H.-C. Chang, M. Marquez, S. L. Suib, and O. Giraldo, Mechanism for helical gel formation from evaporation of colloidal solutions, *Langmuir*, **18**, 8792 (2002).
102. X. Y. Kong and Z. L. Wang, Spontaneous polarization-induced nanohelixes, nanosprings, and nanorings of piezoelectric nanobelts, *Nano Lett.*, **3**, 1625 (2003).
103. H. F. Zhang, C. M. Wang, E. C. Buck, and L. S. Wang, Synthesis, characterization, and manipulation of helical SiO_2 nanosprings, *Nano Lett.*, **3**, 577 (2003).
104. Y. Xin, Z. H. Huang, E. Y. Yan, W. Zhang, and Q. Zhao, Controlling poly(p-phenylene vinylene)/poly(vinyl pyrrolidone) composite nanofibers in different morphologies by electrospinning, *Appl. Phys. Lett.*, **89**, 053101 (2006).

105. M. K. Shin, S. I. Kim, and S. J. Kim, Controlled assembly of polymer nanofibers: From helical springs to fully extended, *Appl. Phys. Lett.*, **88**, 223109 (2006).
106. T. Han, D. H. Reneker, and A. L. Yarin, Buckling of jets in electrospinning, *Polymer*, **48**, 6064 (2007).
107. T. Lin, H. X. Wang, and X. G. Wang, Self-crimping bicomponent nanoribers efectrospun from polyacrylonitrile and elastomeric polyurethane, *Adv. Mater.*, **17**, 2699 (2005).
108. K. Lin, K. N. Chua, G. T. Christopherson, S. Lim, and H. Q. Mao, Reducing electrospun nanofiber diameter and variability using cationic amphiphiles, *Polymer*, **48**, 6384 (2007).
109. G. Larsen, R. Spretz, and R. Velarde-Ortiz, Use of coaxial gas jackets to stabilize Taylor Cones of volatile solutions and to induce particle-to-fiber transitions, *Adv. Mater.*, **16**, 166 (2004).
110. X. F. Wang, B. Ding, J. Y. Yu, M. R. Wang, and F. Pan, A highly sensitive humidity sensor based on a nanofibrous membrane coated quartz crystal microbalance, *Nanotechnology*, **21**, 055502 (2010).
111. S. B. Yang, X. F. Wang, B. Ding, J. Y. Yu, J. F. Qian, and G. Sun, Controllable fabrication of soap-bubble-like structured polyacrylic acid nano-nets via electro-netting, *Nanoscale*, **3**, 564 (2011).
112. X. F. Wang, B. Ding, J. Y. Yu, Y. Si, S. B. Yang, and G. Sun, Electro-netting: Fabrication of two-dimensional nano-nets for highly sensitive trimethylamine sensing, *Nanoscale*, **3**, 911 (2011).
113. X. F. Wang, B. Ding, J. Y. Yu, and J. M. Yang, Large-scale fabrication of two-dimensional spider-web-like gelatin nano-nets via electro-netting, *Colloid Surf. B-Biointerfaces*, **86**, 345 (2011).
114. J. Dyck, The Evolution of Feathers, *Zool. Scr.*, **14**, 137 (1985).
115. R. Grojean, J. Sousa, and M. Henry, Utilization of solar radiation by polar animals: an optical model for pelts, *Appl. Opt.*, **19**, 339 (1980).
116. R. H. Baughman, A. A. Zakhidov, and W. A. d. Heer, Carbon nanotubes-the route toward applications, *Science*, **297**, 787 (2002).
117. D. Li and Y. N. Xia, Direct fabrication of composite and ceramic hollow nanofibers by electrospinning, *Nano Lett.*, **4**, 933 (2004).
118. S. Zhan, D. Chen, X. Jiao, and C. Tao, Long TiO_2 hollow fibers with mesoporous walls: Sol–gel combined electrospun fabrication and photocatalytic properties, *J. Phys. Chem. B*, **110**, 11199 (2006).
119. Y. Zhao, X. Y. Cao, and L. Jiang, Bio-mimic multichannel microtubes by a facile method, *J. Am. Chem. Soc.*, **129**, 764 (2007).
120. Y. Zhao and L. Jiang, Hollow micro/nanomaterials with multilevel interior structures, *Adv. Mater.*, **21**, 3621 (2009).
121. A. Nakajima, K. Hashimoto, T. Watanabe, K. Takai, G. Yamauchi, and A. Fujishima, Transparent superhydrophobic thin films with self-cleaning properties, *Langmuir*, **16**, 7044 (2000).
122. M. Kanehata, B. Ding, and S. Shiratori, Nanoporous ultra-high specific surface inorganic fibres, *Nanotechnology*, **18**, 315602 (2007).
123. M. Guo, B. Ding, X. H. Li, X. L. Wang, J. Y. Yu, and M. R. Wang, Amphiphobic nanofibrous silica mats with flexible and high-heat-resistant properties, *J. Phys. Chem. C*, **114**, 916 (2010).
124. B. Ding, J. H. Kim, Y. Miyazaki, and S. M. Shiratori, Electrospun nanofibrous membranes coated quartz crystal microbalance as gas sensor for NH_3 detection, *Sensor. Actuat. B-Chem.*, **101**, 373 (2004).
125. L. Wannatong, A. Sirivat, and P. Supaphol, Effects of solvents on electrospun polymeric fibers: Preliminary study on polystyrene, *Polym. Int.*, **53**, 1851 (2004).
126. T. Zhao, Z. Liu, K. Nakata, S. Nishimoto, T. Murakami, Y. Zhao, L. Jiang, and A. Fujishima, Multichannel TiO_2 hollow fibers with enhanced photocatalytic activity, *J. Mater. Chem.*, **20**, 5095 (2010).

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