Recent progress in protective membranes fabricated via electrospinning: advanced materials, biomimetic structures, and functional applications

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Abstract

Electrospinning is a significant micro/nanofiber processing technology and has been rapidly developing in the past two decades. It has several applications, including advanced sensing, intelligent manufacturing, and high-efficiency catalysis. We review multifunctional protective membranes fabricated via electrospinning in terms of novel material design, construction of novel structures, and various protection requirements in different environments. To achieve excellent comprehensive properties, such as high water vapor transmission, high hydrostatic pressure, optimal mechanical property, and air permeability, combinations of novel materials containing nondegradable/degradable materials and functional structures inspired by nature have been investigated since decades. Currently, research is mainly focused on conventional protective membranes with multifunctional properties, such as anti-UV, antibacterial, and electromagnetic shielding functions. However, important aspects, such as the properties of electrospun monofilament, development of "green electrospinning solution" with high solid content, and approaches for enhancing adhesion between hydrophilic and hydrophobic layers are not considered. Based on this systematic review, the development of electrospinning for protective membranes is discussed, the existing gaps in research are discussed, and solutions for the development of technology are proposed. This review will assist in promoting the diversified development of protective membranes and is of great significance for fabricating advanced materials for intelligent protection.

Keywords: electrospinning; protective membrane; breathability; waterproof; unidirectional transmission

1. Introduction

Clothing is a significant symbol of humans entering a civilized society. Clothing has protective and aesthetic functions, which are of great significance to human life and behavior. With the development of hi-tech science and technology, the applications and development of protective clothing efficiently guarantee human safety and health in hazardous scenarios.[1, 2] “Protective clothing” refers to clothing with robust properties to protect people from various potentially hazardous factors, such as high temperature, strong wind, heavy rain, chemicals, ultraviolet rays, electromagnetic waves, and viruses, in extreme environments.[3, 4] This goal cannot be achieved by solely relying on traditional textiles and techniques. Therefore, modern technology and industry have constantly put forward new materials, structural designs, and preparation technologies to prepare functional protective clothing.

Conventional protective clothing is usually produced using petroleum-based polymers refined from fossil fuel resources such as oil, coal, and natural gas.[5] In addition, the existing fabrication methods for protective clothing are heat-stretching technology (for preparing expanded polytetrafluoroethylene (e-PTFE)) and classical non-woven processes such as spunbond–meltblown–spunbond (SMS).[6] However, with the development of technology, the disadvantages of these methods are being gradually recognized. First, a significant consumption of thermal and electric energies occur during the fabrication process. Second, the conventional methodology hinders the fabrication of designable nano-/microstructure fibers.[7] Therefore, further progress regarding the development of ecofriendly raw materials, energy-efficient fabrication methods, and constructing multifunctional protective membranes is of great scientific and practical significance. Based on this, advanced electrospinning technology with feasible operation, environment friendly, and energy conservative characteristics has been attracting worldwide attention.

Electrospinning has gained global attention as a method to fabricate unique nano-/microstructures of fibrous membranes. It has diverse applications such as flexible sensing, integrated manufacturing, high-efficiency catalysis, biomedical engineering, and tissue engineering. [8, 9] Various structures, such as core–shell fibers, side-by-side structures, and hierarchical layers, can be easily designed and fabricated by adjusting the equipment.[10] Thus, as a new technology, electrospinning has been applied in protective clothing since 20 years. Significant progress has been made in the development and application of breathable waterproof membranes, unidirectional water transport membranes, and functional protective membranes.[2] Recently, few studies have reported the production of fabrics superior to those produced by few big brands in terms of air permeability, vapor permeability, hydrostatic resistance, and overall moisture management capacity (OMMC). Electrospinning exhibits an excellent adaptability to new structures. It has the characteristic of low energy consumption; thus, the significance of the electrospinning technology in the fabrication of advanced nano-/microfibrous membranes is immense.

The representative products in daily life are breathable-waterproof jackets and medical protective clothing, and the products for anti-UV, anti-bacterial, anti-virus, and electromagnetic shielding have also been studied in recent decades. [4, 11, 12, 13] Considering waterproof and breathable jackets as examples, the global market size of winter-wear functional jackets reached USD 268.3 billion in 2018. The market is expected to grow at a compound annual growth rate of 4.3% from 2019 to 2025.[14] This product is sold by several big brands, such as Gore-Tex, Northface, and TOREAD. Gore-Tex fabric is produced using PTFE by thermal expansion and stretching.[15] With the development of electrospinning technology, few companies have selected electrospun polyurethane (PU) or polyvinylidene fluoride (PVDF) nanofiber membranes. This technological innovation significantly reduces the expense as well as easily endows the product with functionality.[16] The other representative protective product is disposable medical protective clothing, which is mainly used to isolate viruses/bacteria-containing aerogels to prevent cross-infection during medical operations. [4, 13] Disposable protective clothing is usually fabricated using polypropylene (PP) via nonwoven technology. At present, owing to the Covid-19 outbreak, all countries and regions are closely concerned about the use, safety, and supply of medical protective items.[17] Advanced electrospinning technology has innovated this product with multifunctional properties. By adjusting the structure of nanofibers and loading functional materials, the design, preparation, and functionality of medical protective clothing with environment friendly characteristics have been significantly improved.

The electrospinning technology has initiated great innovations in the field of intelligent protective clothing. Therefore, it is necessary and urgent to summarize all the relevant research systematically and comprehensively. However, few challenges remain, including green solvent development, construction of novel bionic structures, and the properties of mono nanofibers, and should be the focus of future research. The impact of the solution to these issues determines the future development of electrospinning in advanced multifunctional protective membranes. Based on the research of electrospinning technology in protective membranes, we will discuss new theories developed, novel materials used, fantastic structures designed, and scenarios applied to functional protective membranes in the following sections. It is believed that this comprehensive review based on the principles, materials, structures, and applications of electrospinning technology can promote the iterative upgrading of intelligent protective membranes.

2. Principle and development of electrospinning

Since the invention of electrospinning, researchers have been exploring the technology and its applications based on numerous materials, including natural macromolecules and synthetic polymers, by optimizing the equipment configuration and adjusting a series of parameters such as the preparation process, materials design, and structure construction.[18] Since the 20th century, after nearly two decades of development, extensive and significant applications in the fields of smart clothing, advanced sensing, and new energy have been realized because of the electrospinning technology. In view of the profound studies conducted on electrospinning, few changes have occurred in terms of definition and theory. Based on the nanofiber-based protective membrane, this section summarizes the current definition, brief history, theoretical development, and critical controlling parameters of electrospinning technology.

2.1. Definition and brief history of electrospinning

Electrospinning is a micro/nano fiber processing technology used to fabricate polymer solutions or polymer melts into fibers under a high electric field. Electrospinning is a particular type of electrostatic spraying.[19] In the electrospinning process, a small droplet is formed under a certain concentration and conductivity; the droplet is then stretched and deformed into a vertebral shape using a high-voltage electrostatic field at the nozzle tip. When the electrostatic repulsive force on the droplet surface exceeds the surface tension, polymer solutions are rapidly ejected from the droplet surface, thereby resulting in electrospun fibers and products.[20] The prepared micro-nanofibers usually have small diameters and large specific surfaces. Additionally, micro-nanofibers with controllable porosity and special micro-morphology can also be designed by adjusting the process conditions and the composition of the polymer solutions. Based on the characteristics of the prepared micro-nanofibers, the prepared products can be used in various applications, such as smart clothing, filtration products, sensors, and tissue engineering, as shown in **Figure 1**.[21]

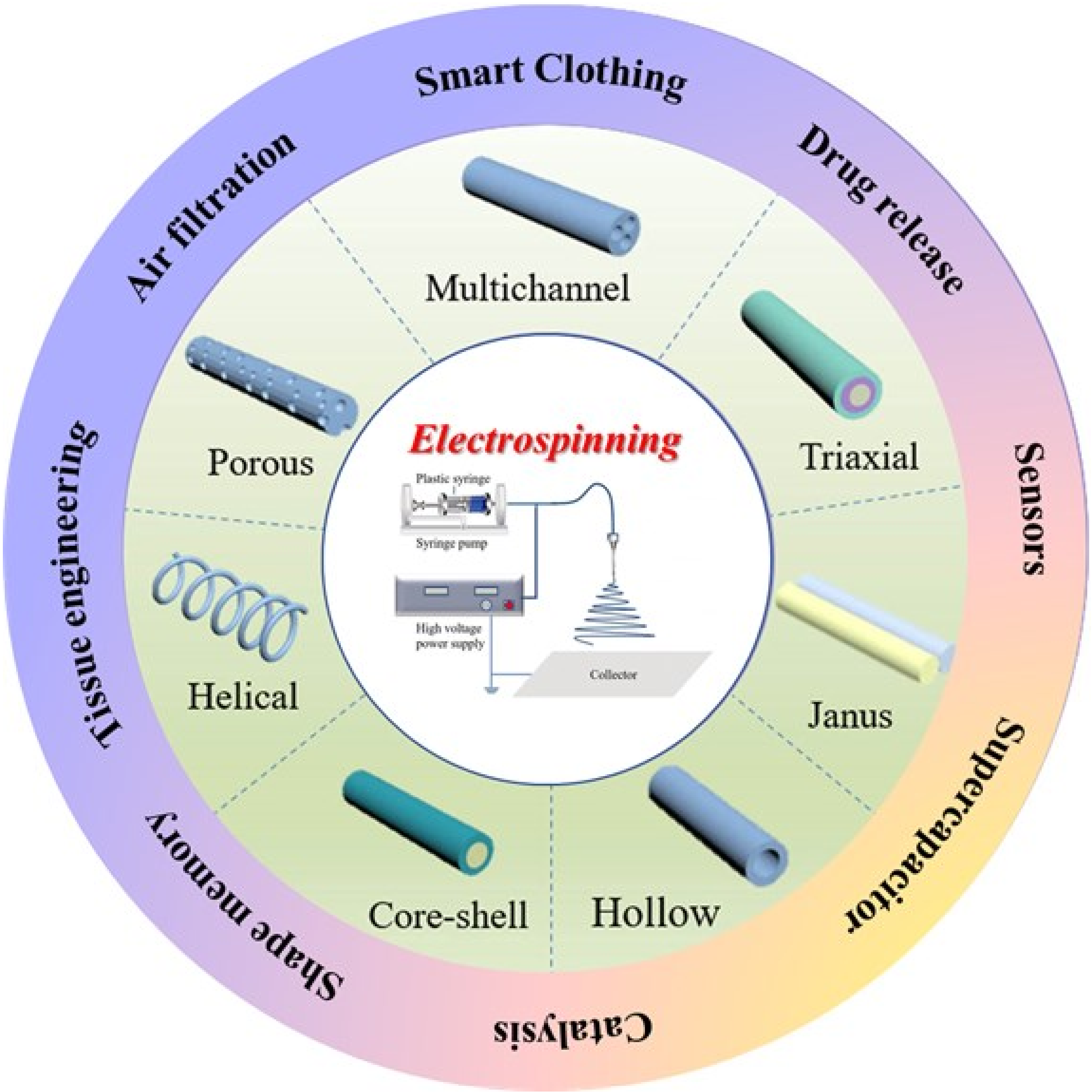

Figure 1. Diverse fiber structures and wide-ranging applications of electrospinning [21]. Reproduced with permission. Copyright 2007, Elsevier.

Electrospinning is a type of electrostatic spraying. Electrospray technology has a long history of over 270 years. In 1745, Bose first obtained a highly dispersed aerosol by applying a high voltage on the fluid surface;[22] in 1882, Rayleigh studied the critical condition for the formation of the jets.[23] He concluded that a jet would be formed when the electrostatic repulsive-force on the surface of the solution is greater than its surface tension; in 1902 Cooley and Morton filed a patent for the process of dispersing volatile liquids by controlling its carried charges;[24] in 1917, Zeleny proposed several basic models to explain the formation of jets, and the author believed that the liquid droplet is in an unstable state when the surface tension of the droplet is not equal to the force applied by the electrostatic field;[25] in 1929, Hagiwara designed a patent for preparing artificial silk via electrospinning technology;[26] in 1934, Formhals described in detail how the polymer solutions forms a jet in the fabrication of polymer fibers by electrospinning, which marks the advent of modern electrospinning technology;[27] in the 1960s, Taylor studied the relationship between the applied static voltage and the angle of the cone on the droplet surface, and he reported the critical interface angle, which is known as Taylor Point, during the electrospinning process;[28] in 1971, Baumgarten studied several processing parameters, such as spinning voltage, feeding speed, solution viscosity, of electrospinning and prepared micro fibers with diameters less than 1 μm;[29] in 1996, Reneker reported the fabrication of nanofibers via electrospinning, and this paper attracted the attention of scientific researchers worldwide;[30] in the 20th century, Ramakrishna et al. performed in-depth research on the electrospinning technology.[31] Ramakrishna et al. published a review paper in 2003 in terms of the electrospinning process, theories, and its applications, which exceeded 5,500 citations (Web of Science).[32] Moreover, in the last 20 years, Bin Ding et al. conducted studies on the various applications of the electrospinning technology. Bin Ding pioneered the electrospinning technology and achieved a fiber diameter of less than 20 nm.[33, 34] A brief history of the development of electrospinning is summarized in **Figures 2A and 2B**. With the development of cutting-edge technology, electrospinning technology has been widely applied in several fields such as smart fabrics, filter materials, and new energy sources.

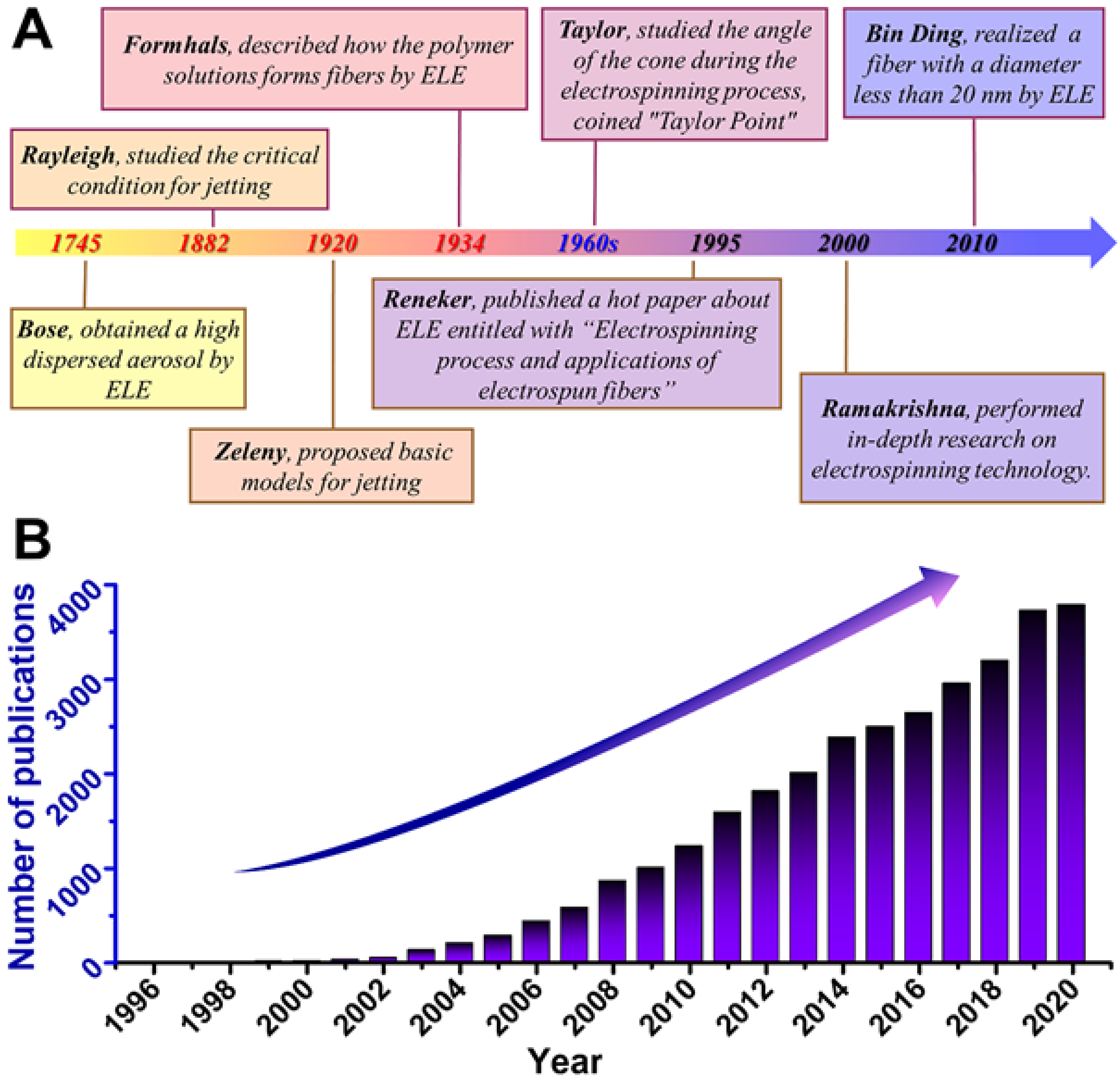

Figure 2. Brief history and the development of electrospinning (ELE). A) Brief history of electrospinning; B) Number of publications in recent two decades (Data get from Web of Science by searching the key word of electrospinning).

2.2. The principle and the theory of electrospinning

Electrospinning is a type of electrostatic spraying. Electrostatic spraying refers to the phenomenon in which tiny droplets are ejected when the liquid is applied at a high voltage over a specific critical voltage. The basic setup of the electrospinning process is shown in

Figure 3A. When the electrostatic spraying liquid is a polymer solution or melt, the ejected liquid may exhibit a favorable continuity at certain viscosity, temperature, and humidity conditions, allowing for continuous electrospinning, as shown in **Figure 3B**. **Figure 3C** shows three models of electrostatic spraying for preparing micro-nano structured aerosols or polymer particles.

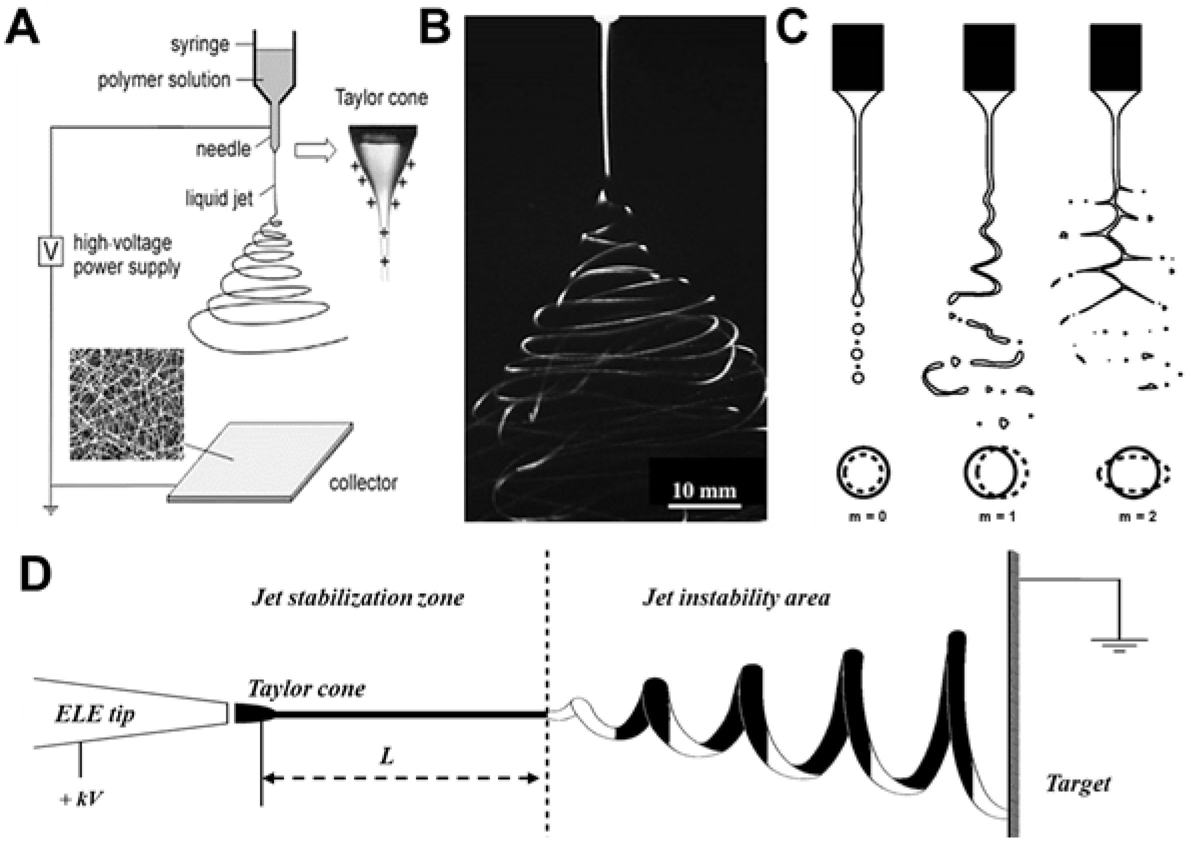

Figure 3. The principle and theory of electrospinning. A) Basic setup of electrospinning. The insets show a drawing of the electrified Taylor cone and a typical scanning electron microscopy (SEM) image of poly (vinyl pyrrolidone) (PVP) nanofibers.[35] Reproduced with permission. Copyright 2004, John Wiley and Sons/Wiley-VCH. B) A snapshot of an electrospinning jet with well-developed loops from the nozzle.[36] Reproduced with permission. Copyright 2007, Elsevier. C) Three jet break-up modes, the axisymmetric varicose break-up, the lateral kink break-up, and the ramified jet break-up.[37] Reproduced with permission. Copyright 2000, Elsevier. D) the stabilization zone and instability area of electrospinning.

This critical condition for electrospinning is that the surface electrostatic repulsive force of the polymer solution is equal to its surface tension. In this condition, the polymer jet cone, which is known as the Taylor cone, is formed with a specific angle at the nozzle end. During electrospinning, the surface of the droplet accumulates charges. A repulsive force is generated on the surface, and the surface tension of the droplet is the reaction force of the repulsive force. The interaction between the pair of forces determines whether the electrospinning process will be conducted. Theoretically, the difference between the surface tension of the droplet and its repulsive force, ΔP, is given by Equation 1.[38, 39]

$$\Delta P = \frac{2\gamma}{R} - \frac{e^2}{32\varepsilon_0\pi^2R^4}, \tag{1}$$

where γ is the surface tension ($\mathrm{mNm^{-1}}$), R is the radius of the droplet (m), e is the charge amount of the droplet (C), and ε_0 is the dielectric constant ($\mathrm{F\ m^{-1}}$).

Four factors, surface tension, the radius of the droplet, the charge amount of the droplet, and the dielectric constant, affect ΔP. Increasing the surface tension and dielectric can increase ΔP, while increasing the charge amount of the droplet will decrease ΔP. The influence of the radius of the droplet on ΔP is more complex and depends on three other factors. In the critical state, namely Rayleigh stability limit, the electrostatic repulsive force on the surface is equal to the surface tension, the droplet is in a balanced state, and the droplet follows Equation 2. [23, 40] Furthermore, John W. S. et al. designed an instrument for quantitative measuring the charge to mass ratios of the drops at the Rayleigh stability limit. Authors found that drops at breakup obey this equation within a standard deviation of 4%.[41]

$$\frac{e}{M} = \sqrt{\frac{288\varepsilon_0\gamma}{\rho^2D^3}}, \tag{2}$$

where ρ is the density of the droplet ($\mathrm{kg\ m^{-3}}$), M is the mass of the droplet (kg), and D is the charge density on the surface of the droplet ($\mathrm{C\ m^{-2}}$).

With an increase in the intensity of the electric field, the number of charges on the surface of the droplet gradually accumulates. When the repulsive force is greater than the surface tension, jetting occurs. Based on the quantitative study of the critical voltage in terms of different liquids, like water, glycerin, and transformer oil during the process of electrospinning, Taylor analyzed the effects of various factors such as voltage, plate spacing, and feeding ratio of the jetting during the electrospinning process of polymer solutions, and determined the critical voltage, V_c, of the jetting from the tip of Taylor's cone as follows.[42]

$$V_c^2 = \frac{4H^2}{L^2}\left(Ln\frac{2L}{R} - \frac{3}{2}\right)(0.117\pi\gamma)R_0, \qquad (3)$$

where H is the distance between the plates (cm), L is the distance between the nozzle and the supporting plate (cm), and R_0 is the radius of the nozzle (cm).

Furthermore, Taylor claimed that the semi-vertical angle of the cone at the stable state is 49.3° for any conducting solution.[28] However, this value can be different for different polymer solutions and melts. Reznik, Yarin et al. have observed that it can be ≤ 33.5°.[38, 43] The cone shape also depends on the applied voltage and the solution feed rate. Although Taylor’s model might only be consistent with some specific cases, his equation can still predict the required critical voltage.

When the jetting is ejected from the Taylor cone, the pristine jet is stretched into finer branches of jetting. Then, jet moves through the collection distance with solvent evaporation and finally solidified on the collecting plate. During the process, jetting can be divided into stable and unsteady flight sections.[44] In the unstable region, the jet moves at a high speed and is further stretched under the electric field, as shown in **Figure 3D**. Correspondingly, the fiber diameter decreases rapidly in this process. Simultaneously, with the evaporation of the solvent, polymer solution solidifies into micro/nanostructured fibers.

Besides these classic theories, the modeling and simulation of electrospun nanofibers in the past decades also have been developed.[45, 46] Based on these theoretical foundations, like mass conservation, electric charge conservation, momentum balance, Ostawald-de Wale power law, constitutive equation, researchers have constructed Slender body model, Electrohydrodynamic model, Spivak & Dzenis model, Reneker model, Stability theory, Electromagnetic model, and others for deep understanding and accurate prediction of the electrospinning.[46, 47] Many factors, such as multi-field effects, control parameters, surface charge density, etc. in the actual electrospinning process have been carefully considered in developed theoretical models. These studies well formulate the process of electrospinning regarding the droplet formation, whipping, bending, Rayleigh instabilities, etc. in a quantitative perspective. Basic properties of electrospinning, such as jet radius and fiber diameter can be predicted by them.

Based on the above theoretical analysis, the characteristics of the polymer solution and the processing control parameters are essential in electrospinning. These factors significantly influence the performance of electrospinning products.

2.3. Factors for the processing of electrospinning

The three factors that significantly influence the electrospinning process and the final product can be classified as follows: first, the characteristics of the polymer solution, including polymer molecular weight, solution viscosity, surface tension, conductivity, and solvent volatility; second, the processing parameters, including applied electrostatic voltage, feeding speed, collection distance, and nozzle diameter; and third, environmental conditions, including temperature and relative humidity. The integrative action of these three types of factors determines the fiber morphologies and properties, such as fiber diameter, fiber surface roughness, porosity, and stress, as summarized in Table 1.[48] It should be emphasized that these three types of factors usually affect each other.

Table 1. Factors influencing the characteristics, morphologies, and properties of electrospinning nano/microfibers.

Influence Factors	**Properties of electrospinning nanofibers**
Polymer	
1. Molecular weight	1. Proper molecular weight is required
2. Molecular Distribution ↑	2. Possibility to obtain beaded nano fibers ↑
3. Solubility ↑	3. Beneficial for preparing electrospun fibers
Solutions	
1. Volatility ↑	1. Appropriate volatility is important for obtaining fibers
2. Surface tension ↑	2. Diameter ↑; possibility to obtain beaded filament ↑
3. Dielectric constant ↑	3. Generate fibers with uneven diameters ↑
4. Conductivity ↑	4. Diameter of electrospinning fibers ↓
Collector	
1. Quiescent disk	1. Random fibers; low physical property
2. Rotating cylinder	2. Aligned fibers; high physical property
Environment	
1. Humidity ↓	1. Morphology becomes uniform, and the diameter reduces
2. Temperature ↑	2. Assists in the electrospinning process

↑ indicates increase; ↓ indicates decrease

The relative molecular weight of the polymer determines the properties of the polymer, including the glass transition temperature, melting point, mechanical strength, and solubility. The polymer requires a proper molecular weight for a favorable spinnability; otherwise, a low molecular weight will cause an electrostatic spray and consequently fail to obtain the fibers. The diameter of the fiber obtained shows an increasing trend as the relative molecular weight of the polymer increases. The viscosity of the polymer solution also affects the electrospinning process. Generally, high molecular weight polymers are required to prepare an electrospinning solution with a lower concentration. The diameter of the fiber increases cubically with increasing concentration of the polymer solution.[49] The dielectric constant, conductivity, volatility of the solution, and solubility of the solvent also affect the morphology of the electrospun fibers. When the dielectric constant of the solution is high, the surface of the jet can accumulate more charges, thereby resulting in several smaller jets and fibers of varying diameters, and with a higher conductivity of the polymer solution, electrospun fibers with smaller diameters can be obtained.[50] Solvents with extremely high or low boiling points are not suitable for electrospinning. Solvents with low boiling points lead to the blockage of the nozzle, thereby hindering the spinning process. However, solvents with higher boiling points are not conducive to the solidification of the polymer fibers during the spinning process. Unique fiber structures with different roughness, porous surfaces, and flat cross-sections can be prepared by adjusting the mixed solvent system.[51] Additionally, the surface tension of the polymer affects the electrospinning process. The surface tension of a polymer is generally affected by numerous factors, such as the polymer solution, solvent, solution concentration, temperature, and humidity.[52]

The processing parameters in the electrospinning process can be controlled to prepare products with functional properties. The static voltage in the electrospinning process determines whether electrospinning can be performed. The applied static voltage to the solution must exceed a certain threshold so that the charge repulsion on the jet is greater than the surface tension, thereby ensuring the progress of electrospinning. Increasing the static voltage can increase the charge density on the jet surface, consequently reducing the jet radius. Thus, the diameter of the prepared fiber tends to decrease. A feeding ratio that is too high or too low will cause instability of the Taylor cone, which affects the morphology of the obtained fiber.[53] In contrast, an increase in the feeding ratio leads to an increase in the diameter of the fibers, while an excessively high feeding ratio may cause the melting bonding of the fibers. The ideal receiving distance is also significant for the preparation of the electrospun fibers. The collection distance requires to be equal to the evaporation rate of the solvent to obtain electrospun fibers with an ideal morphology. In addition, the temperature and humidity of the environment affect the surface tension of the spinning solution and the diffusion process of the solvent; thus, the environmental conditions also significantly affect the electrospinning process and the product performance. Reducing the humidity of the environment will assist the solvent diffusion process. The obtained fiber morphology is more uniform, and the diameter of the fiber is also reduced. In contrast, increasing the temperature of the environment can reduce the concentration and surface tension of the polymer solution, which can contribute to the electrospinning process.[54]

Significantly, the quantitative investigation of electrospinning regarding the relationship between control parameters and fiber morphology also has been focused on. [55, 56-58] We notice that there are some improvements in research methods of quantitative analyses. Previous quantitative research methods, like orthogonal experimental design and using power law relationships are time-consuming, and low efficiency in optimization the process of electrospinning.[57, 59] At present, these deficiencies have been solved greatly by innovative methodologies, like Response Surface Methodology (RSM) and Artificial Neural Network (ANN) in which all important factors are varied together over a set of experimental runs.[56, 60, 61] These new methods are more reliable and rapid, importantly, which can capture the interaction effects between different parameters. Therefore, the total number of experiments and experimental cost can be dramatically reduced. [57, 61, 62] These methods have significantly contributed to the theoretical progress, quantitative investigation, and efficient optimization of the electrospinning. Specifically, recent quantitative research mainly focuses on the influence of various important parameters, such as solution concentration, applied voltage, spinning distance, volume flow rate, etc. on mean fiber diameter and standard deviation of fiber diameter. RSM and ANN are widely used methods which can find simultaneous effects of various electrospinning parameters on fibers. Related research has been applied to diverse polymers, like PAN, PA, PS, PMMA, PVDF, PVA, PLA, starch, and silk fibroin. [58, 63, 64, 65] Through these quantitative analyses, essential characteristics of electrospun fibers, such as fiber morphology, porosity, and roughness can be well controlled, and these studies offered an in-depth insight into the complex phenomena of electrospinning. Furthermore, these comprehensive studies based on mathematical and theoretical analyses provide a solid theoretical foundation for the stable fabrication, and industrialization of electrospinning. Thus, these fundamental investigations have important guidance for the future development of electrospinning.

In general, the polymer solution, electrospinning processing parameters, and environmental conditions affect the electrospinning process, as well as the product morphology and performance. By controlling these factors, the electrospun fibers and their final products with different morphologies and structures can be designed and prepared to meet various functional applications.

2.4. Industrialization and products of electrospinning

Nanofibers prepared by electrospinning technology have a high specific surface area, high porosity, easy size control, and easy functionalization. It was predicted that the global market of nanofiber products will grow from $927 million in 2018 to $4.3 billion by 2023 at a compound annual growth rate of 36.2% according to BCC research, global markets, and technologies for nanofibers. Electrospinning technology mainly includes the solution method and the melting method, and the solution method currently accounts for most nanofibers produced. Solution electrospinning has the characteristics of low cost and feasible operation; thus, it is the predominant method used for laboratory research and industrial production of nanofibers. The following will be discussed based on equipment improvement, industrialization, and related products of electrospinning.

Solvent-based electrospinning can be divided into needle-based and needleless categories. In the laboratory, electrospinning equipment with needles is often used because of its easy operation, high stability, and feasible reconfiguration, as shown in **Figure 4A and 4B**. [66] However, the production rate using this typical electrospinning technology is usually approximately 0.01–1 g h^{-1}, which is much lower than the requirement for industrial production. [67] Therefore, to improve the yield of electrospinning, highly efficient multi-needle electrospinning devices, which combine multiple needles together and spin nanofibers simultaneously, have been developed.[68] Using this technique, the production efficiency of electrospinning can be increased; however, the increase is not sufficient to meet the requirements of industrial mass production. Additionally, this method can cause new problems such as electric field interference between multiple needles, which can be minimized by using an auxiliary electrode and a special arrangement of needles, as shown in **Figure 4C, and 4D**. Further, in 2003, as a milestone in fiber production, researchers designed a rotating cylindrical drum with dots in the solution as the starting surface for fiber generation. [66, 69] Later, the technology was upgraded to needleless electrospinning equipment. Needleless electrospinning systems significantly improve the spinning efficiency and overcome the limitation of clogging during the spinning process. Using needless equipment, the production rates can reach 8.6 g h^{-1} with a cylinder for polyvinyl alcohol fibers.[70] The Elmarco company (Liberec, Czech Republic) produced the first industrial needless electrospinning setup (Nanospider®) and claimed that the equipment has a production rate of 1.5 g min^{-1} per meter of roller length for fabricating nanomembranes with diameters of 50–500 nm, as shown in **Figure 4E**.[71] The needleless electrospinning system significantly improved the spinning efficiency and overcame the limitation of clogging during the spinning process. However, the configurations of the jets were not easy to control because its processing is sensitive to humidity and temperature, and the products were usually more uneven than those of needle-based electrospinning. Overall, solution electrospinning has the limitation of residual organic solvent. In the electrospinning process, usually approximately 90% of the solution is used to prepare polymer solutions, which can potentially cause environmental pollution and is a health hazard to workers. Meanwhile, residual toxic solvents restrict the use of related products in biomedical and tissue engineering applications. Therefore, in recent years, researchers have developed solvent-free electrospinning and melt electrospinning. In brief, this method involves heating the polymer to a temperature above its melting point and then stretching the polymer melt solution into fibers under a high electric field; this is the most promising method for nanomembrane production. Chen Mingjun et al. reported that the scale-up production line of melt electrospinning can achieve a capacity of 300–600 g h^{-1}.[72] In addition, melt electrospinning can assist the electrospinning of non-soluble polymers, such as PP, polyethylene, and polyphenylene sulfide, as shown in **Figure 4F**. However, this type of electrospinning method requires external heating and other auxiliary equipment. This type of solution consumes more energy than the solvent-based electrospinning. In addition, this technology is still under development. The preparation and research of protective films by melt electrospinning has rarely been performed.

To realize industrialization, additional to simple operation and low cost, continuous production and stable quality control are also required. To date, there are few products based on electrospinning technology in the market. Common electrospinning-based products are air filters (ProTura® Nanofiber, United Air Specialists (a Clarcor company); Smart Mask, NASK), and medical devices (Bioweb™, Zeus). However, research on electrospinning technology in areas such as energy, oil–water separation, catalysis, and advanced protective clothing require to be continuously focused on. It is believed that solutions based on basic principles to overcome the challenges of industrialization will be provided in the future, and more electrospinning products will be available in the market. In this review, we focus on electrospinning protective membranes based on advanced material modification, bionic structure design, and diverse applications to explore the development of electrospinning in recent years.

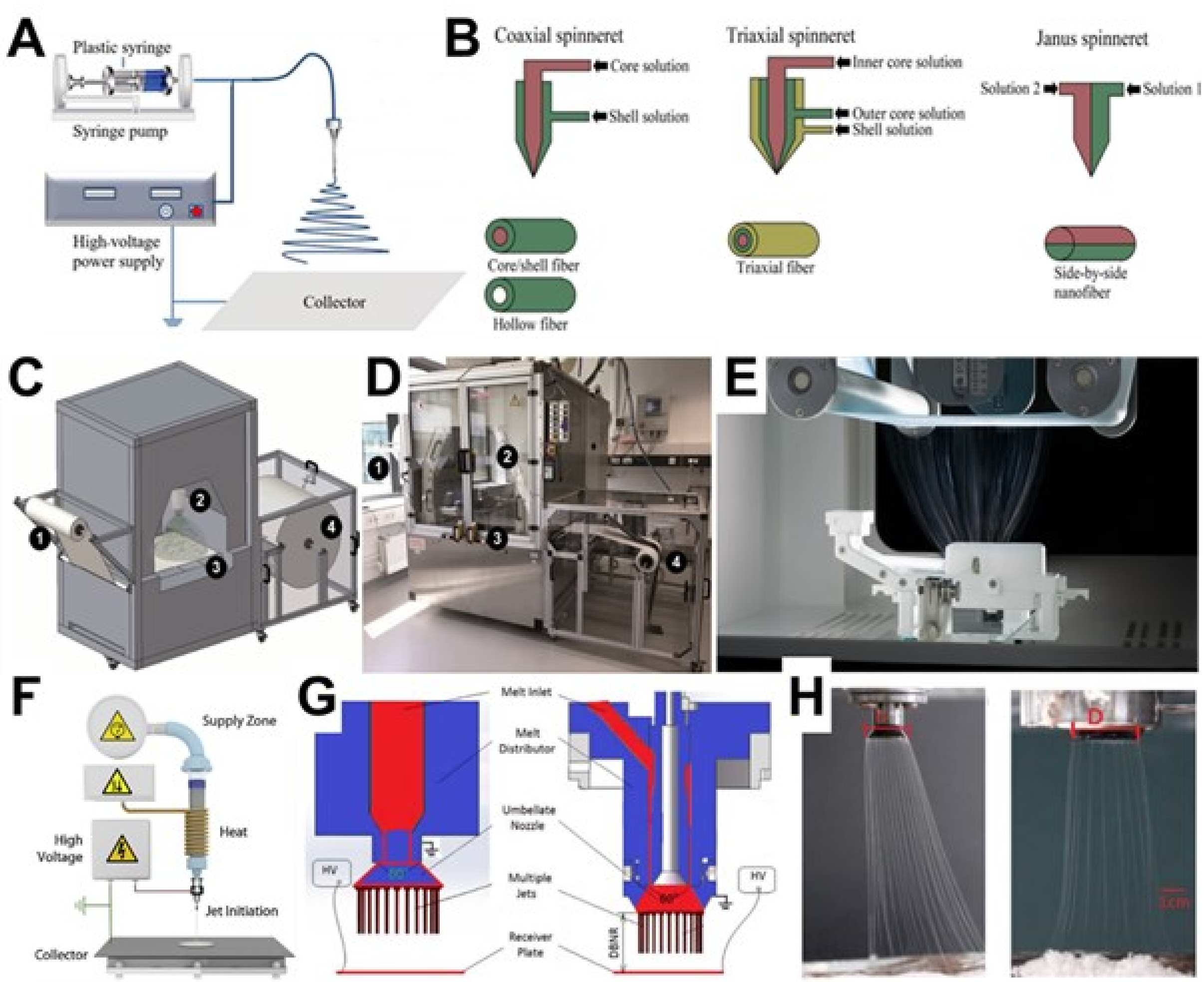

Figure 4. The development of the electrospinning equipment from laboratory and industry. A) The typical solvent-based electrospinning equipment in laboratory scale.[21] Reproduced with permission. Copyright 2020, De Gruyter. B) Re-configuration of the needle of the electrospinning equipment for constructing diverse nanofiber structures.[66] Reproduced with permission. Copyright 2020, John Wiley and Sons/Wiley-VCH. C) Model and D) photo of the pilot-scale electrospinning equipment for fabrication of silk nanofibers.[73] Reproduced with permission. Copyright 2020, MDPI. E) Electrospinning processing of the needleless electrospinning in pilot-scale (Nanospider^{TM} Technology; Elmarco Ltd.). F) Schematic of melt electrospinning onto a static collector.[74] Reproduced with permission. Copyright 2016, Elsevier. G) Schematics and photographs of melt differential electrospinning applied using two types of nozzles (HV: high voltage; DBNR: the distance between nozzle and receiver); H) Nozzle with melt distributed on the outer surface of the umbrella-like nozzle and nozzle

with melt distributed on the internal surface of the umbrella-like nozzle.[75] Reproduced with permission. Copyright 2014, John Wiley and Sons/Wiley-VCH.

3. Classification of fibrous membrane by materials

The material used is a key factor in determining the final performance of the product. In recent years, researchers have classified materials used for fabricating protective membranes according to the design and utilization of electrospinning materials. It was observed that the use of hydrophobic materials, among which PVDF and fluorinated thermoplastic polyurethane (TPU) are the representatives, in the protective film is of high significance. In addition, considering their excellent processing performance, polyacrylonitrile (PAN)-based electrospinning protective films have also been studied. However, PAN is not generally used on its own, and additional hydrophobic post-treatment is required to construct a protective membrane. In addition to the basic mechanical properties and hydrophilic/hydrophobic properties, researchers have paid more attention to the essential protective properties, such as air permeability, moisture permeability, one-way transport capability, and hydrostatic pressure, of the fibrous membrane. Based on in-depth research on high-performance protective films and the continuous development of a series of products, protective films have been widely used in personal thermal management, high-performance combat clothing, and various other protection fields.

3.1. PVDF-based protective membrane

PVDF is a thermoplastic fluoropolymer that can be synthesized by the polymerization of vinylidene fluoride. Compared to other fluoropolymers, such as PTFE, PVDF has a lower density of 1.78 g cm^{-3}. It combines the functionalities of fluor resin and general engineering resin; therefore, it possesses favorable elasticity, low weight, low thermal conductivity, chemical resistance, high temperature resistance, oxidation resistance, weather resistance, radiation resistance, and piezoelectricity.[76] It also shows excellent properties, such as electrical properties, dielectric properties, and thermoelectric properties, required for the electronics industry.[77] It is the second most produced fluorine-containing plastic and has a wide range of applications in smart fabrics, biomedicine, advanced sensors, new energy, and defense industries.

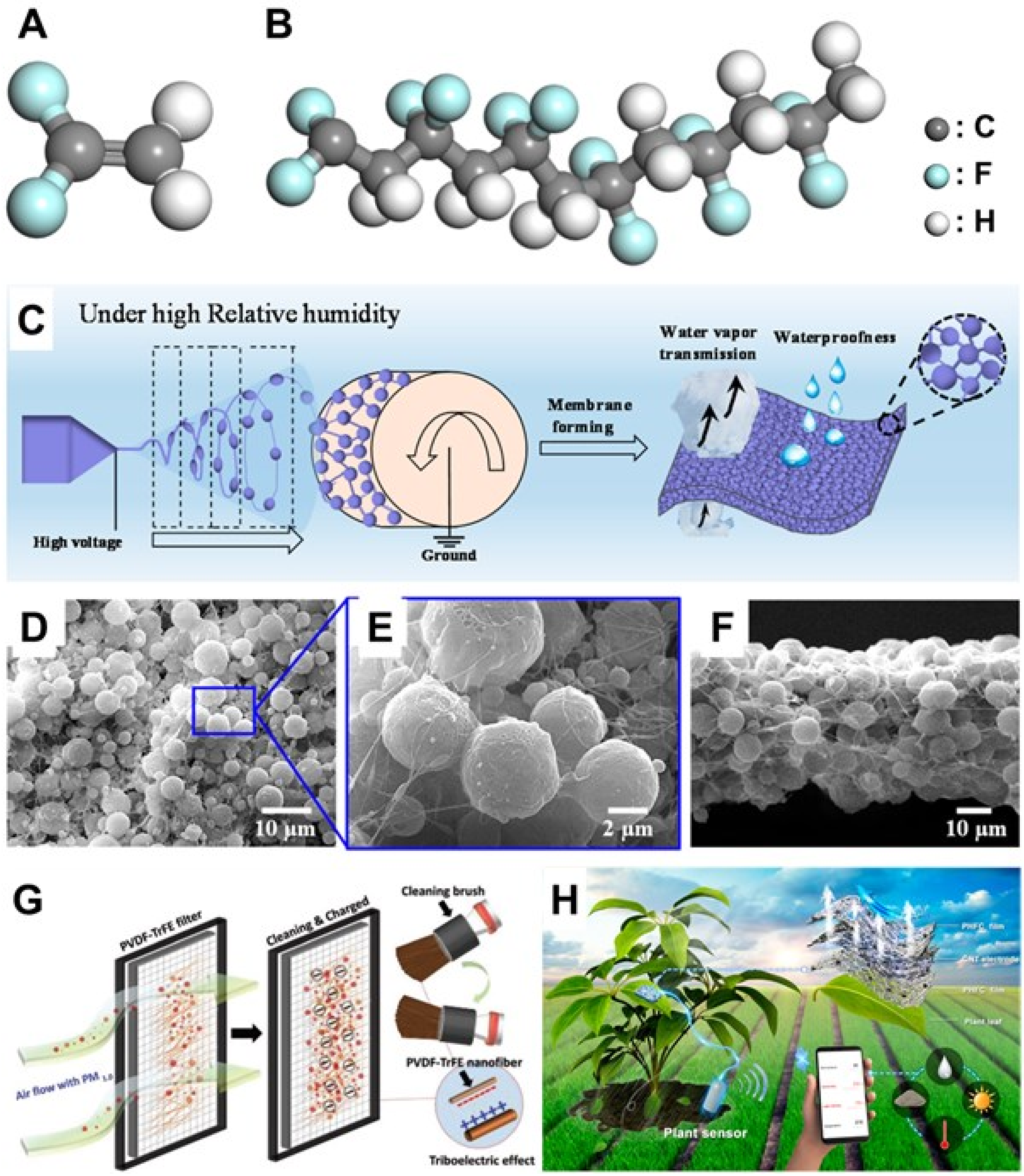

Figure 5. Representative research of protective membranes based on PVDF. A) Monomer of PVDF, vinylidene fluoride. B) Polymer chain of PVDF. C) schematic of the fabrication process of superhydrophobic PVDF membrane. D) and E) top-view and F) cross-section of PVDF membrane.**[78]** Reproduced with permission. Copyright 2018, American Chemical Society. G) Illustration of the triboelectrically charged PVDF–trifluoroethylene (TrFE) filter for enhanced trapping of particulate matter $(PM)_{1.0}$.**[79]** Reproduced with permission. Copyright 2019, John Wiley and Sons/Wiley-VCH. H) schematic of breathable membranes for an on-plant self-powered sustainable agriculture system.**[80]** Reproduced with permission. Copyright 2021, American Chemical Society.

Currently, the most widely used waterproof and breathable fabric is Gore-Tex, which is a two-way stretched porous PTFE. PVDF has a chemical structure similar to that of PTFE, which has good processing properties and stable hydrophobic properties. Therefore, it can be used to fabricate advanced waterproof and moisture-permeable fabrics by electrospinning. In 2002, Chang et al. first reported a composite fibrous membrane based on PVDF and conductive carbon nanotubes (CNTs). This study investigated the basic characteristics, such as viscosity, electrical conductivity, and surface tension, of PVDF/N, N-dimethylformamide solutions with different concentrations of CNTs.[81] The results showed that a fiber with a diameter as small as 70 nm could be obtained. However, other important properties, such as breathability, water vapor transmission (WVT), and waterproofness, have not been discussed. In 2017, a PVDF-based breathable waterproof membrane was systematically investigated by Ding Bin et al., in which the authors proposed a method for improving the mechanical properties of membranes by bending polyvinyl butyral (PVB) and heat post-treatment.[82] Related studies are shown in **Figure 5**. The mechanical properties of PVDF were superior to than that of the pristine PVDF membrane by a factor of approximately four with a high tensile stress of 10.5 MP and a WVT of 10,600 g $(m^2 \cdot d)^{-1}$. However, the hydrostatic pressure decreased with increasing PVB concentration. Subsequent studies on blending hydrophobic fluorinated PU (FPU) into PVDF and improving the mechanical properties of PVDF by hot pressing have been reported, and the waterproof and moisture permeability properties were systematically studied. Current research remains focused on balancing these two fundamental properties, that is, achieving high water moisture permeability and high hydrostatic pressure resistance. It is worth mentioning that these comprehensive properties of the electrospun membrane depend on the diameter and morphology of nanofibers. Thus, related quantitative research has been conducted. For example, Salehi M. et al. studied the influence of control parameters on mean fiber diameter, diameter distribution, and porosity of the PVDF membrane by RSM and ANN. [58, 83] Results presented that the fiber diameter and standard deviation of fiber diameter decrease with the increase of PVDF composition and increase with the increasing solution concentration. The porosity decreases with the increase of the solution concentration. Recently, in 2018, Li J. et al. systematically investigated properties of PVDF fibrous membrane with seven parameters: voltage, flow rate, and rotation rate, tip to collector distance, concentration of PTFF, concentration of PVDF, and mass ratio of DMAc to acetone via RSM. The authors well optimized the electrospinning process and membrane distillation performance by adjusting corresponding variables.[84] These studies are of great significance for improving and optimizing the overall properties, including mechanical property, air permeability, and hydrostatic pressure resistance of PVDF-based electrospun products.

In addition, based on the favorable vapor permeability and flexibility of electrospinning membranes, PVDF-based electrospinning has been applied to triboelectric energy harvesting, sensors, and face mask filters. In 2019, Kyung Seok Han et al. used PVDF–TrFE to fabricate an air filter with high efficiency (94% for particulate matter $(PM)_{1.0}$ filtration). It was reported that the filter efficiency can be improved from 88% to 94% by the polarization of dipoles and triboelectrification, as shown in **Figure 5G**.[79] In 2021, Prof. Ying et al. designed a hydrophobic triboelectric nanogenerator (TENG) based on electrospinning technology. A film with nanofibers and microspheres was prepared by electrospinning PVDF–hexafluoropropylene and electrospray F-CNT, as shown in **Figure 5H**. This unique structure allows the film to possess excellent air permeability and hydrophobicity. Its highest output power density can reach 330 mW cm^{-2}.[80] Prof. Ding et al. designed a wearable TENG based on nanofiber membranes using PVDF/ polydimethylsiloxane (PDMS) and PAN/PA6, which can provide current and voltage outputs up to 110 μA and 540 V. It is worth mentioning that the designed generator exhibits excellent performance in a highly humid environment.[85] Simultaneously, Prof. Ding et al. studied a tailorable, washable, and breathable power generation fabric based on PVDF electrospinning. The fabric can obtain biomechanical energy from human movement and effectively convert it into electrical energy. The output power density of the electrospinning-based textile reached 80 mW m^{-2}. The design provides a clean, safe, and efficient way to drive wearable electronic devices. In addition, the smart fabric can also be used as a high-sensitivity sensor for human movement.[86] Power generation protective membranes can benefit from sensors, smart textiles, face masks, and next-generation wearable electronics. Notably, key scientific issues in this field are mainly to solve the high output power density of triboelectricity and the stability of devices in complex environments (such as in a high-humidity environment). The solution to related issues will significantly promote the development of intelligent protective films.

In recent years, some studies have investigated multifunctional PVDF membranes to ensure the basic performance of PVDF, such as favorable waterproofing and moisture permeability. PVDF membranes with UV-resistant properties can be achieved by blending organic and inorganic anti-UV additives, and the membranes can be endowed with thermal management performance by adding phase-change materials into polymeric matrix.[87] Flexible and breathable PVDF-based electrospun membranes with high-sensitivity properties and energy harvesting characteristics can be fabricated by utilizing the piezoelectric/triboelectric properties of PVDF materials and electrospinning technology. Considering the rapid development of smart clothing and the generation of novel energy sources, PVDF-based waterproof and moisture-permeable clothing produced by electrospinning has a promising future.

3.2. PU-based protective membrane

PU is a polymer containing repeating units of urethane (–OCO–NH–) segments. Bayer first synthesized PU in 1937.[88] Generally, PU is obtained by the addition reaction of polyether, polyester diol, polyol, and isocyanate, followed by reaction with a chain extender. Representative research related to electrospun PU for protective membranes is shown in **Figure 6**.[89] Because PU has favorable designability, weather resistance, and biocompatibility, among synthetic materials, PU has the widest range of applications.[90] The following four fields accounts for 73% of the global PU consumption: furniture, construction, electronics, and automobiles.

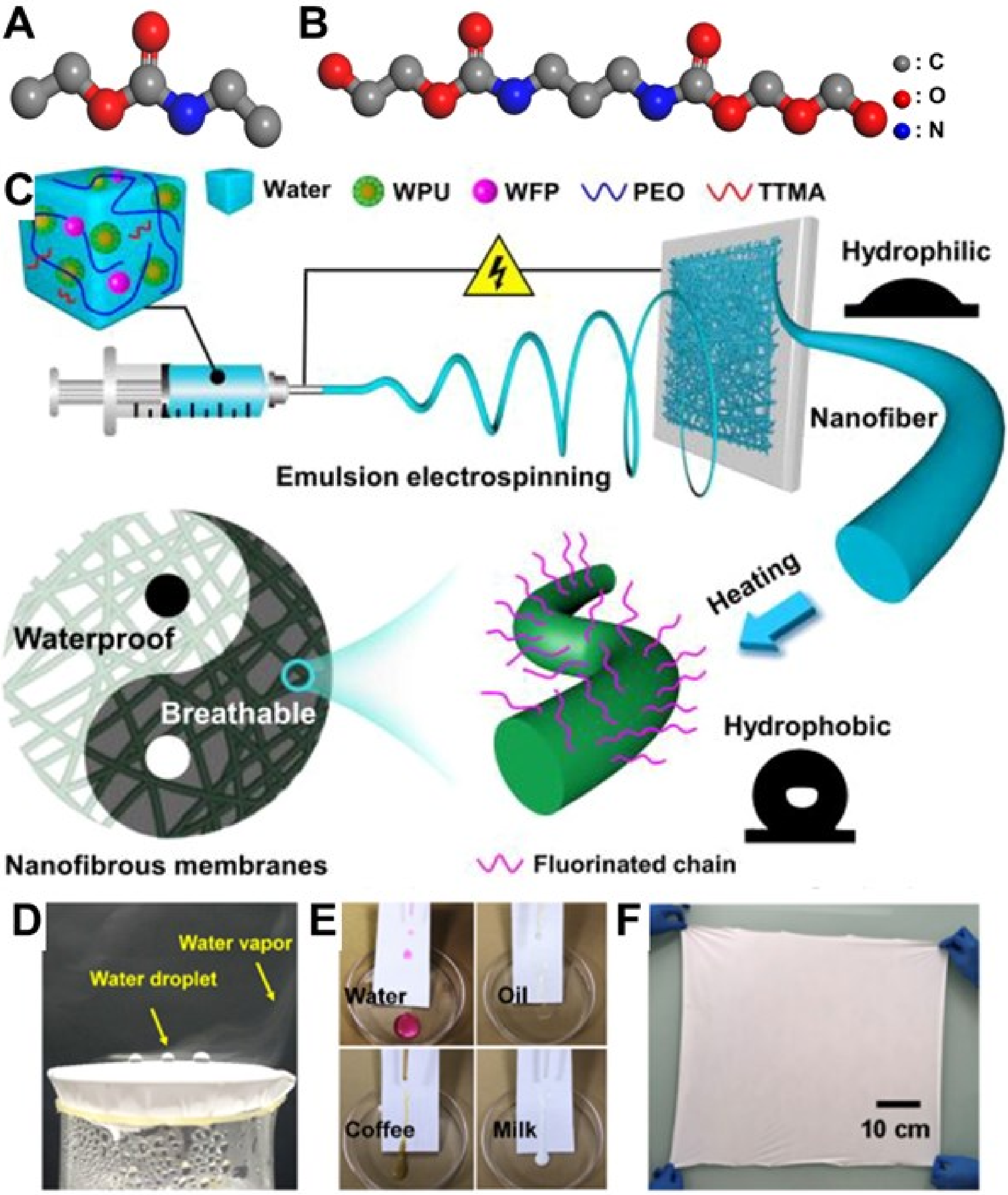

Figure 6. Representative research of protective membrane based on TPU. A) Typical group of PU (–OCO–NH–). B) Typical polymer chain of PU. C) Schematic diagram of environmentally friendly waterborne PU nanofibrous membranes by emulsion electrospinning for waterproof and breathable textiles.[91] Reproduced with permission. Copyright 2022, Elsevier. D) Demonstration of waterproof and breathable performance; E) Lyophobic property; F) Large-scale product photograph of the PU/C6FPU-2/$MgCl_2$-3 fibrous membrane.[92] Reproduced with permission. Copyright 2017, American Chemical Society

Because the structure of PU can be flexibly designed and its processing performance is excellent, electrospinning products have been widely studied. Yun Kyung Kang reported the first breathable waterproof PU membrane in 2007, and optimized various conditions of electrospinning, such as PU concentration, applied voltage, and tip-to-collector distance, to develop waterproof and breathable electrospun nanofibers onto substrate fabrics.[93] The obtained PU nanofibers/fabrics exhibited favorable air permeability, vapor transmission, and thermal insulation properties; however, the hydrostatic pressure resistance of PU nanofibers/fabrics cannot reach that of resin-coated fabrics. In 2015, Li et al. reported a composite fibrous membrane, in which terminal FPU and CNTs endowed the membrane with superhydrophobicity.[94] The optimized membrane possessed an excellent hydrostatic pressure of up to 108 kPa, a WVT over 9,200 g $(m^2 \cdot d)^{-1}$, and a low tensile stress stress of 12.5 MPa. Subsequent research focused on improving its mechanical properties and waterproof performance by blending FPU and hydrophobic PDMS, and hydrophobic nanoparticles, such as titanium dioxide, silicon dioxide, and graphene oxide.

Since 2017, an increasing amount of research has been conducted on PU-based unidirectional water-transit products. Researchers usually fabricate two or more layers with different hydrophilic and hydrophobic properties to achieve unidirectional water transmission. In 2018, Miao et al. reported a tri-layered fibrous membrane based on hydrolyzed PAN-SiO_2, hydrophobic PU, and hydrolyzed PU–PAN.[95] The membrane can achieve guided water transportation from the inner to the outer layer, which shows a high one-way transport index, R, of 1,021% and a hydrostatic pressure of 16.1 cm H_2O; R is an important factor considered in this research. However, when considering some of the comprehensive properties of the film, such as mechanical strength, hydrostatic pressure resistance, durability, and the interaction force between the hydrophobic and hydrophilic layers, there are several issues related to material structures that require to be resolved.

The theory for the air permeability and moisture permeability of the protective membrane is worth mentioning. The air permeability of nanofibrous membranes obeys Darcy's law,[96] which can be expressed as follows in Equation 4.

$$v = k \cdot \frac{\Delta p \cdot \varepsilon^3}{x \cdot A^2 \cdot (1-\varepsilon)^2}, \tag{4}$$

where v is the air velocity, k is the air permeability coefficient, Δp is the pressure difference across the nanofibrous membranes, and ε, x, and A are the porosity, thickness, and surface area of the membrane, respectively.

Considering the design of electrospinning protective membrane, the air permeability of the membrane can be improved by controlling the porosity and thickness of the membrane. Additionally, considering that the protective membrane should be equipped with a high hydrostatic pressure, the high-performance protective membrane should have the characteristics of smaller pore size and higher porosity.

The water vaper permeability of the protective membrane was driven by the moisture concentration difference between the two sides of the membrane. Therefore, moisture transmission through the nanofibrous membrane follows Fick's law of diffusion.[97] In particular, the WVT of the electrospinning membrane can be described using Equation 5.

$$WVT = D \cdot \frac{\varepsilon}{\tau} \cdot \frac{\partial c}{\partial x}, \tag{5}$$

where D is the water vapor diffusion coefficient, τ is the tortuosity factor of the membrane, c is the water vapor concentration, and ∂c/∂x is the water vapor concentration gradient.

Tortuosity is the ratio of the radius of the average pore size to the membrane thickness. Therefore, the pore size and porosity of the membrane are important factors that affect the vapor permeability and moisture permeability of the protective membrane. Therefore, Amir Rabbi and co-workers quantitatively investigated the porosity and fiber diameter of the TPU electrospun membrane by RSM and ANN. Results showed that the validity of the RSM (R^2 =

0.988) and ANN model ($R^2 = 0.990$) are both well enough for predicting morphology of fibers. Particularly, the concentration of TPU solution plays a significant role (relative importance of 79.85%) on fiber diameter and its standard deviation.[98] Recently, in 2017, Mohsen Gorji et al. utilized the RSM to optimize the overall performance, including water vapor permeability (WVP), air permeability (AP), and mechanical property of the TPU eletrospun membrane. Statistical results (ANOVA) indicated that $R^2 = 0.99$ for WVP, $R^2 = 0.96$ for AP, $R^2 = 0.99$ for tensile strength at break. Experimental results are in good agreement with the model values by RSM.[99] The construction of the one-way water transportation and the quick-drying membrane was on the basis of these theories, and in the following sections, we will discuss these aspects.

At present, research on waterproof and breathable electrospun membranes based on environmentally friendly waterborne PU (WPU) has also attracted increasing attention from scholars, as this methodology has the potential to help overcome the limitation of organic solvents caused by traditional processes. In 2021, Zhou et al. designed a type of protective waterproof-breathable nanomembrane based on WPU materials and water-based fluoropolymer by post-crosslinking. The achieved membrane exhibited an excellent WVT of 12.8 kg m^{-2} d^{-2}, hydrostatic pressure of 74.3 kPa, and high elasticity of 67.4%, as shown in **Figure 6C**.[91] Then, the author further studied waterborne electrospinning based on WPU, long-chain alkyl polymer, and polycarbodiimide (PCD) for waterproof and breathable protective membranes. The crosslinking reaction between PCD and WPU was designed to enhance the mechanical properties of the membranes. The result indicated that the broken stress of the achieved membrane can reach approximately 10 MPa, which is much higher than that reported previously.[100] Compared with the traditional organic solvent electrospinning system, the aqueous electrospinning system has environmentally friendly characteristics; thus, there is no issue of significant solvent pollution. However, the aqueous electrospinning system generally involves the electrospinning of an aqueous PU system. The formulation of the spinning solution is more complicated than that of a traditional organic electrospinning system. The control of the temperature and humidity during the electrospinning process is more significant than organic electrospinning system. In addition, the mechanical strength of nanofiber membranes spun from aqueous systems is low, and post-treatment processes, such as cross-linking reactions, are usually required. In general, water-based electrospinning systems are still under development, and more attention should be focused on the development of high-performance water-based polymers, the design of high-solid water-containing polymers, and the controllable adjustment of the hydrophilic and hydrophobic properties of the water-based polymer interface.

Recently, based on the porosity of electrospinning products, functional studies on PU electrospinning, such as warmth retention and flame retardancy, have been conducted. In 2021, Wu et al. designed an ultralight and mechanically strong fibrous sponge with excellent warmth retention with a low thermal conductivity of approximately 25.8 mW m^{-1} K^{-1} and a low volume density of approximately 2.2 mg cm^{-1} via direct electrospinning and thermal crosslinking. For the material design, PU and polysulfone were used as the polymer matrix, and a blocked isocyanate polymer was used as a crosslinker to enhance the mechanical properties.[101] The limitation of this study is that only one factor in thermal management, which is the thermal conductivity, was considered. Recent research on the application of textiles in thermal management has been attracting significant attention. For example, in 2019, Prof. Cui et al. designed a PE-based nanofiber membrane for cooling management.[102] The most important aspect of this paper is that he proposed an important factor, infrared (IR) management (IR transmission and IR reflection) that requires to be considered for thermal management. For example, coating a reflective metal layer in a traditional fabric or an electrospinning membrane, such as silver nanowires, can increase the radiation efficiency and enhance the thermal retention property.[103] In fact, there are numerous factors, such as heat convection, moisture evaporation rate, and textile intelligent deformation to stimulus, all of which affect the heat transmission and absorption of the product.[104]

In summary, with the development of wearable textile materials, in recent years, an increasing number of researchers have focused on PU-based electronic skins, antibacterial protective membranes, and thermal management fabrics based on electrospinning technology.[105] These studies have broadened the application range of electrospun films. However, functional design membranes with high hydrostatic pressure resistance, high mechanical strength, high one- way transport property, and adaptable moisture permeability are still important research topics for further studies.

3.3. PAN-based protective membrane

PAN is a polymer obtained by the radical polymerization of acrylonitrile monomers. Pure PAN is brittle and hard, and its glass transition temperature is approximately 95 °C. It can be softened and decomposed at 220–300 °C. PAN fiber was made into spun fibers by DuPont in 1942.[106] PAN fibers are more inexpensive than natural fibers, and they exhibit superior sunlight resistance and excellent anti-insect performance. PAN is also an important raw material for preparing carbon fiber and has important applications in aircraft, missiles, and pressure vessels.

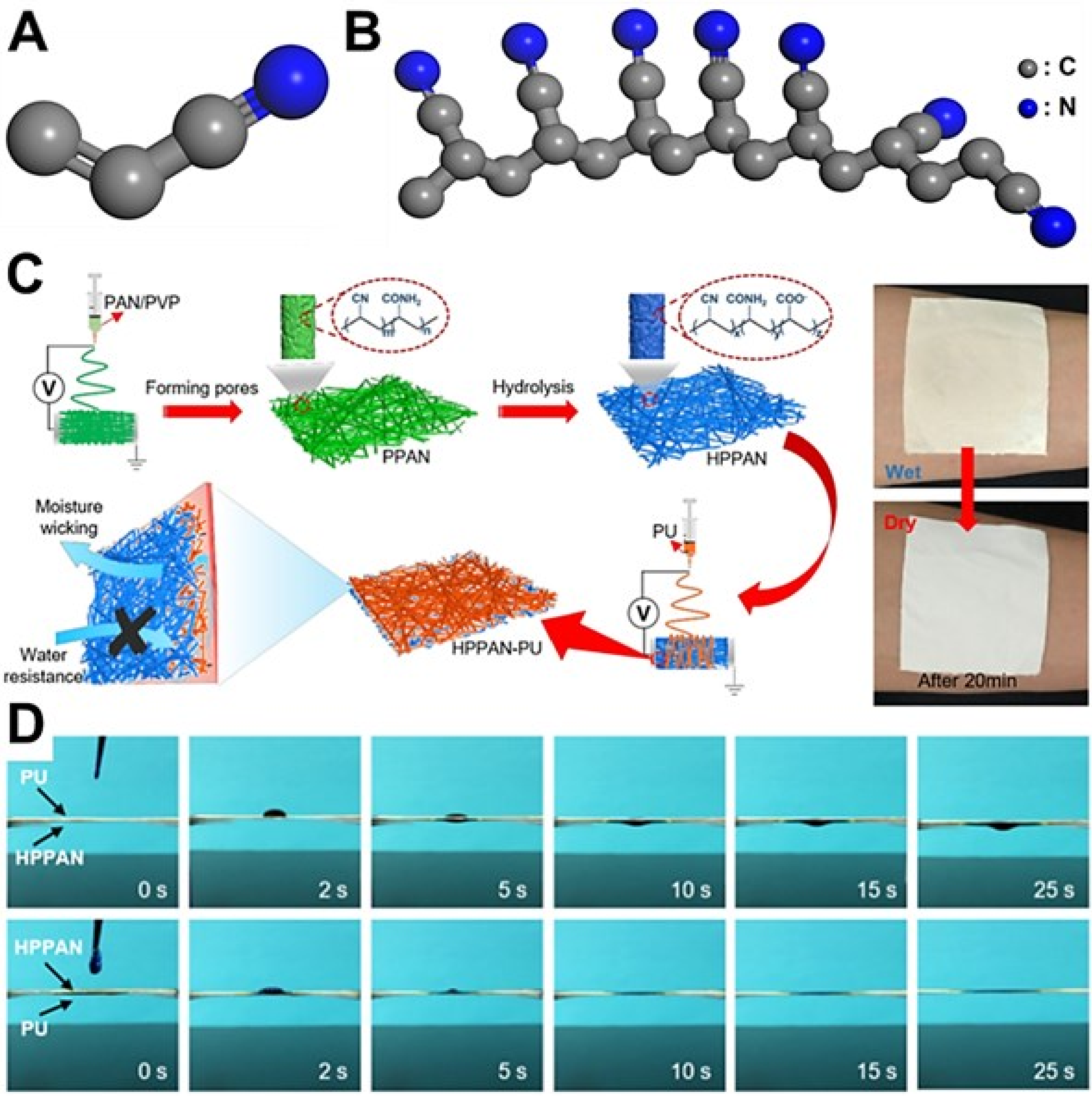

Figure 7. Representative research of protective membrane based on PAN. A) Monomer PAN, acrylonitrile. B) Polymer chain of PAN. C) Schematic of fabrication of dual layer PU/ hydrolyzed porous polyacrylonitrile (HPPAN) membranes and optical images showing rapid drying feature of PU/HPPAN membranes. D) Digital demonstration of water transport behavior on the two-sided PU/HPPAN nanofiber composite membrane.[107] Reproduced with permission. Copyright 2020, Elsevier.

The representative research on PAN in electrospinning technology for protective membranes is shown in **Figure 7**. In 2002, Drew et al. first reported the electrospinning of PAN for application in photovoltaic cells. The author considered that the PAN material fabricated by electrospinning can achieve a specific surface area that can help generate a high photocurrent.[108] The first report on PAN-based waterproof and breathable membranes was in 2014. Wang et al. used waterborne FPU to enhance the hydrophobicity of PAN via coating.[109] The overall performance of the resultant membranes was significantly enhanced; the membrane possessed a high hydrophobicity with a water contact angle (WCA) of 159°, a high hydrostatic pressure of 83.4 kPa, and a high WVT of 9,200 g $(m^2 \cdot d)^{-1}$. Sheng et al. developed a chemical modification method to enhance the mechanical properties of fibrous membranes.[110] In this study, the author constructed a PU/PAN/PVB electrospinning membrane, in which a blocked isocyanate prepolymer (BIP) was added as the cross-linker. After a chemical cross-linking reaction, the overall mechanical property of this composite membrane significantly improved to 33 MPa, which is higher than that of the pristine PU/PAN membrane by a factor of three. Babar et al. reported a dual-layer surface which was treated by a nonwoven/electrospinning nanofiber membrane based on PAN and hydrophilic SiO_2 nanoparticles. The optimized membrane possesses a high one-way transport index of 1,413% and an excellent OMMC of 0.99.[111] In a subsequent study, Miao et al. developed a theoretical model and the corresponding quantitative analysis on the design of a fast-drying membrane, that is, the wicking velocity (*v1*) and spreading velocity (*v2*) satisfy the following equations.[112]

$$v1 = \frac{\rho g r^2}{8\mu} \exp\left(-\frac{\rho^2 g^2 r^3}{16\mu\gamma cos\theta} t\right), \tag{6}$$

$$v2 = \sqrt{\frac{r\gamma cos\theta}{4\mu t}}, \tag{7}$$

where ρ is the liquid density, g is the acceleration of gravity, r is the radius of the channel, μ is the viscosity of the liquid, γ is the surface tension of the liquid, and θ is the contact angle between the liquid and inter-fiber channel.

Significantly, the authors input the parameters into Equations 6 and 7, they observed that the quantitatively calculated wicking and spreading velocity was consistent with the experimental results. Therefore, vertical wicking and horizontal spreading can be controlled by the anisotropic driving forces between the inter-fiber channels, which can be designed by controlling the hierarchical structures in different layers. Correspondingly, the progress of quantitative study in terms of PAN electrospinning also has been widely investigated. For example, Bentolhoda H. M., Shu- Ying Gu, Ramazan A. A., and co-workers used methods of regression analysis, RSM, and ANN to analyze the influence of electrospun parameters on the fiber morphology, porosity, and contact angle of the PAN fibrous membrane. RSM displayed a good accuracy in predicting the porosity while ANN can much accurately predict the contact angle. [65, 113] The applied voltage and the solution concentration are key parameters that affect the porosity. The solution concentration is the critical parameter that determines the contact angle and the fiber diameter of the membrane. These studies have theoretical and practical value for guiding the controllable fabrication of the electrospun membrane. They can facilitate the PAN-based fibrous membrane applied in advanced water-directional transport.

In addition, based on the triboelectric properties of PAN electrospun membranes, few researchers have studied their applications in protective masks and self-powered human motion monitoring systems. In 2021, Yang Jiang et al. reported self-powered all-nanofiber-based TENGs with UV-protective, self-cleaning, and antibacterial properties by electrospinning Ag nanowires (NWs)/TPU nanofibers and TiO2@PAN networks. This device has the functions of mechanical energy harvesting and self-powered sensing.[114] Guo and Xiong fabricated a series of PAN-nanofiber-based facial masks with high flow rates, filtration efficiencies, and long-lasting antibacterial effects, which are available for the personal protection during the Covid-19 outbreak.[115]

Overall, in recent years, research on PAN-based protective membranes has focused on endowing functionalities, such as superhydrophobicity, self-cleaning ability, UV resistance, and self-powered systems. In addition, few studies have attempted to combine an electrospun moisture-permeable fibrous membrane with unidirectional water transmission to form an advanced functional membrane. At present, the one-way transport capacity of over 1,000% can be achieved, but achieving a high hydrostatic pressure remains a challenge. Designing a unique hierarchical structure and learning from nature is necessary to resolve the contradiction between unidirectional moisture permeability and high hydrostatic pressure resistance.

3.4. Other materials-based protective membranes

In addition to the traditionally used materials of PVDF, PU, and PAN discussed above for application in waterproof and moisture-permeable membranes, other materials, such as aromatic polyamide,[116] poly (styrene–butadiene–styrene) (SBS),[117] and cellulose, [118, 119] are selected as waterproof and moisture-permeable materials because of their unique properties.

Aromatic polyamide materials usually possess good thermo-resistant characteristics, so the materials prepared using these materials can be used in high-temperature conditions. Park et al. developed m- aramid-based nanofibrous membrane, which showed a favorable WVT of 7,650 g $(m^2 \cdot d)^{-1}$ and relatively lower thermal shrinkage than commercially produced e-PTFE. Zhang et al. investigated an SBS-based membrane, and confirmed that the obtained membrane showed excellent wrinkle resistance and tensile fatigue resistance. [120, 121] Additionally, considering the flexibility of SBS, Zhijun Ma et al. recently explored SBS-based electronic skin. In this study, a stretchable conductor (over 1,800% strain) was fabricated by coating an SBS-based electrospun fibrous membrane with a liquid metal. The obtained devices exhibited high stretchability, permeability, and conductivity.[122] In addition, considering sustainable development, traditional petroleum-based materials are not easily degradable, so new waterproof and moisture-permeable materials, such as cellulose and chitin, are being focused on.[123] According to reports, its waterproofing and moisture-permeable performance can be comparable to those of Gore-Tex and Next care. Furthermore, based on the basic properties of the material, hydrophobic materials such as PDMS,[124] fluoroalkyl silane,[125] and SiO_2,[126] can be used as doping components to improve the hydrophobic properties of the raw materials. Therefore, a membrane with hydrophobic properties and a high hydrostatic pressure can be achieved.

Meanwhile, the sustainable development of electrospinning based on materials and dissolution is also a concern for several researchers. In 2021, Zhou et al. reported a type of protective clothing using polyamide and ethanol via electrospinning. The obtained membrane had integrated properties with a high hydrostatic pressure of 32.4 kPa, high particle removal efficiency of 99.9%, WVT of 11.2 kg m^{-2} d^{-1}, air permeability of 2.6 mm s^{-1}, and tensile stress of 15.6 MPa.[127] He et al. designed a new multi-functional bioprotective mask via green electrospinning. In the fabrication process, 5-bromosalicylic acid and PVB were used as the polymer matrix, and ethanol was used as the electrospinning solvent.[128] Considering the development of materials in biomedical applications, we have noticed that quantitative investigations of electrospinning based on diverse biomaterials, like PLA, PCL, PEO, PVA, gelatin, chitosan, starch, silk, etc. have received wide attention.[64, 129] This fundamental research will greatly promote the fabrication and optimization of bio-based nanofibers. Meanwhile, combined with green solvent used and these biomaterials, the problem of toxic organic solvent remain can be solved. These studies will not only propel the industrialization of electrospinning, but also impel electrospinning membranes applied in high added-value biomedical applications, like wound healing, tissue regeneration, and drug delivery.

Overall, waterproofness, water moisture permeability, particle removal efficiency, and unidirectional water permeability are important functionalities of the protective items. To overcome the trade-off relationship between these key properties and improve its comprehensive performance, the consideration of aspects such as material design, structure construction, and post-treatment is required. Detailed discussions are presented in the following sections. Additionally, the spinnability of the material, design of the high solid content solution, development of green solvent, and compatibility of the material and electrospinning equipment are important factors that require to be considered during laboratory experiments and industrial production.

4. Material modification and structure design of membranes

Apart from the impact of material properties on the protective film, structures, such as roughness of the fiber surface, and different construction methods of multilayer films, are also important factors that affect the overall performance of the protective film. In particular, the hydrostatic pressure resistance and water repellency of the protective film are significantly affected by the hydrophilic/hydrophobic and structural characteristics. Among the numerous studies on the structure of the protective film, the researchers mainly analyzed and studied the comprehensive performance of the protective film based on two aspects: fiber morphology and the construction of multilayers. Research on the control of fiber roughness includes blending hydrophobic nanoparticles and constructing intrinsic hydrophobic polymer chains; research based on the construction of multilayers includes the construction of differential hydrophilic/hydrophobic layers, adjustment of multilayer structure, and bionic structure simulation. Based on the research on structure design, several reports inspired by the simulation of natural fiber structures have emerged. These studies demonstrate favorable comprehensive functionalities, including high mechanical properties, favorable moisture permeability, excellent unidirectional moisture conductivity, and high resistance to hydrostatic pressure, which provide the foundation for the future development of protective fabrics for intelligent skin, wearable sensing, and new energy sources.

4.1. Modifying hydrophilicity/hydrophobicity

From the viewpoint of the material, general engineering polymers, such as PVDF, PAN, and TPU, can be used to fabricate electrostatic spinning protective fabrics. However, considering the comprehensive performance, such as hydrostatic pressure resistance, mechanical strength, and moisture permeability, raw materials with hydrophobic properties are required to construct high-performance protective products.

Hydrophilicity/hydrophobicity is an essential characteristic of materials, which is determined by the molecular structure of the material, as shown in **Figure 8A and B**. Hydrophilic structures are molecular structures that are easily polarized so that water molecules can form hydrogen bonds with it, and hydrophobic structures are structures with molecules that repel water molecules, consequently hindering the formation of hydrogen bonds.[130] Theoretically, hydrophobic molecules tend to be nonpolar. Therefore, they can be dissolved in neutral and nonpolar solutions. The contact angle (θ) between the material and water is a crucial parameter that reflects the hydrophilic and hydrophobic properties of the materials, while θ obeys Young's equation as follows.[131]

$$\gamma^{SV} = \gamma^{SL} + \gamma^{LV} cos\theta, \tag{8}$$

where θ is the contact angle, γ^{SL} is the solid/liquid interfacial free energy, γ^{SV} is the solid surface free energy, and γ^{LV} is the liquid surface free energy.

In addition, the roughness of the interactive surface between the material and water also affects θ. An increase in the material roughness can enhance the hydrophobicity of the material. The relationship between the material roughness and θ is expressed by the following Cassie equation:[132]

$$cos\theta^{*} = \Phi_1 cos\theta_1 + \Phi_2 cos\theta_2, \tag{9}$$

where θ^* is the apparent contact angle of the heterogeneous surface, θ_1 and θ_2 are the contact angles on the two homogeneous surfaces, Φ_1 and Φ_2 are surface fractions of the solid domains 1 and 2, respectively.

In the Cassie equation, the contact angle on the air domains is $\theta_2 = 180^o$, $cos\theta_2 = -1$; hence, the apparent contact angle can be simplified as Equation 10.[133]

$$cos\theta^* = -1 + \Phi_1(1 + cos\theta_1), \tag{10}$$

Thus, for a very rough surface, $\Phi_1 \ll 1$; hence, θ^* tends to 180^o, and the drop will detach from the material surface. Hence, when designing high-performance protective fabrics, there are generally two approaches to improve the hydrophilic/hydrophobic properties of the material: 1) selecting materials with differentiated hydrophilic and hydrophobic properties; and 2) adjusting the surface roughness of the material to improve the hydrophilic and hydrophobic properties.[134] The hydrostatic pressure resistance of the fibrous membrane is an important parameter for protective products to determine its serviceable range. The high hydrostatic pressure resistance enables the use of the product in extreme environments such as heavy rain and deep water. Theoretically, the hydrostatic pressure resistance of the porous film satisfies Equation 11:[135]:

$$\triangle P' = -\frac{4\gamma}{d_{max}} cos\theta_{adv}, \tag{11}$$

where $\triangle P'$ is the pressure that is enough to extrude water through the fibrous membrane, γ is the surface tension between water and the surface of the membrane, θ_{adv} is the contact angle between water and the membrane, and d_{max} is the maximum pore diameter of the fibrous membrane.

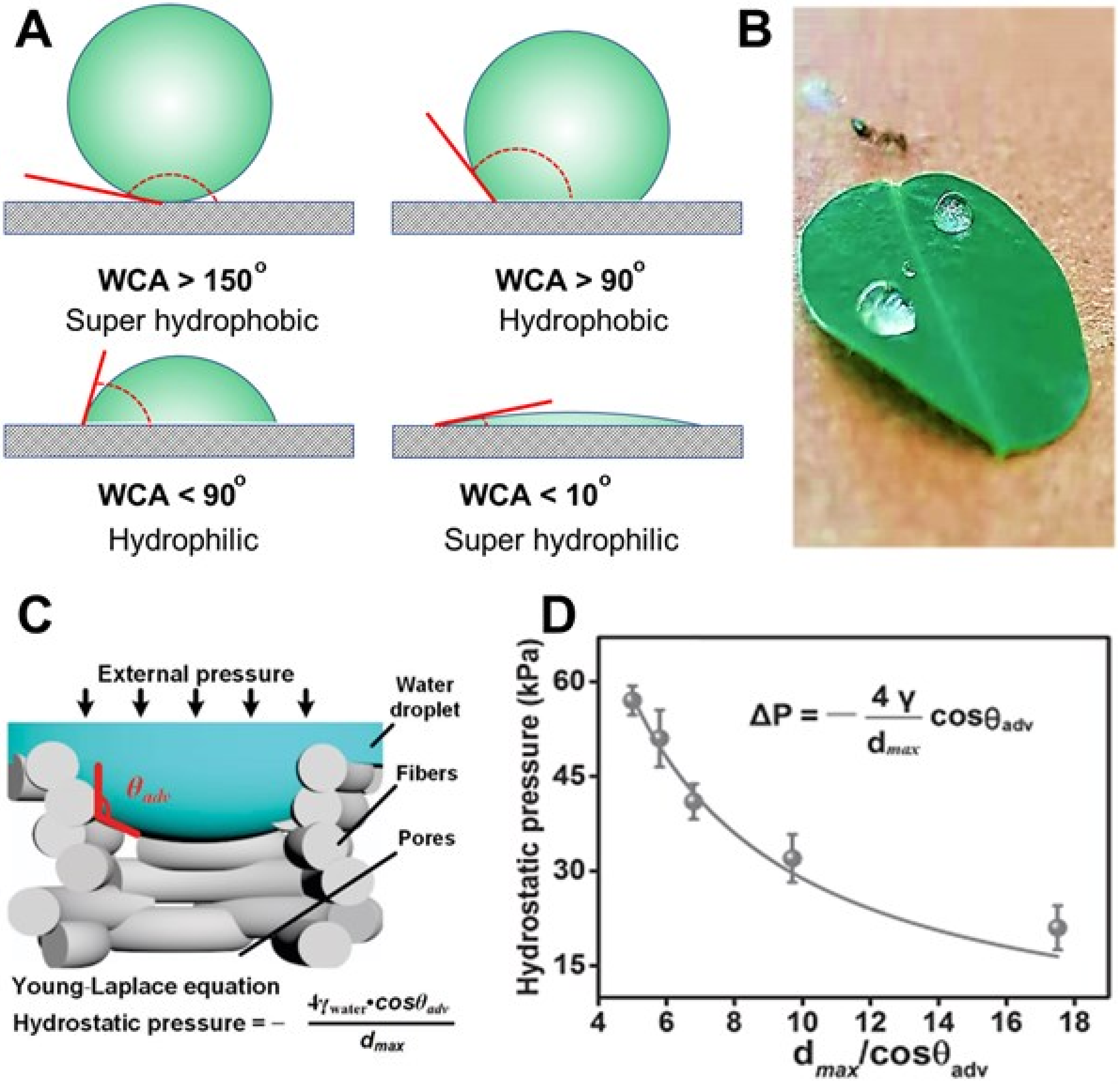

Figure 8. Hydrophobicity and hydrophilicity of materials as well as the relationship between hydrophobicity and hydrostatic pressure. A) WCA of different types of surfaces; B) Hydrophobic phenomenon of leaf surface in nature. C) The proposed mechanism of waterproof property based on Young–Laplace equation.[135] Reproduced with permission. Copyright 2016, John Wiley and Sons/Wiley-VCH. D) Young–Laplace law for hydrostatic pressure, d_{max} and θ_{adv}.[82] Reproduced with permission. Copyright 2014, Springer.

The hydrostatic pressure resistance of the film is affected by the contact angle of the material and the pore size of the membrane. Theoretically, the hydrostatic pressure resistance is inversely proportional to the pore size and is directly proportional to the value of cos θ, as shown in **Figure 8C**. Therefore, a hydrophobic material should be selected to construct a high-performance protective film. Hence, the mainstream protective membrane on the market, the super-hydrophobic e-PTFE, Gore-Tex, is constructed based on this principle, as shown in **Figure 8C and 8D**. Considering the facile processing characteristics of materials for electrospinning, hydrophobic materials, such as PVDF and fluorinated TPU, are widely studied for constructing protective products. Cui et al. reported a multilevel fibrous membrane based on FPU and PVDF by the blending method, where the hydrostatic pressure of the membrane can be improved by bending FPU to 140 kPa, and with a broken stress of 13 MPa, a WVT of 11,300 g $(m^2 \cdot d)^{-1}$.[136] Zhao et al. reported an overall waterproof performance and breathable nanomembrane based on FPU. FPU with short perfluorohexyl ($-C_6F_{13}$) chains were introduced into a PU solution for electrospinning, and magnesium chloride was used to decrease the pore sizes of the fabrics. The achieved membranes possessed a favorable broken strength (12.4 MPa, high WVT (11,500 g $(m^2 \cdot d)^{-1}$), and excellent hydrostatic pressure (104 kPa), thus satisfying the requirements for high performance in harsh environments.[92] In other studies based on the hydrophilic PAN electrospinning membrane, a high-performance protective film can be prepared by coating a layer of hydrophobic material. Sheng et al. reported a fluoride-free PAN-based breathable waterproof membrane by PDMS modification. PDMS assists the fiber to form a hydrophobic adhesive structure which can improve the waterproofness and breathability of the electrospun membrane.[93] The modified PAN membranes demonstrated a favorable hydrostatic pressure (80.9 kPa, tensile stress (15.7 MPa, high WVT (12,500 g $(m^2 \cdot d)^{-1}$), and an air permeability of 9.9 mm s^{-1}. Therefore, the fluorine-free protective film is a future development trend that considers both technological development and environmental protection.

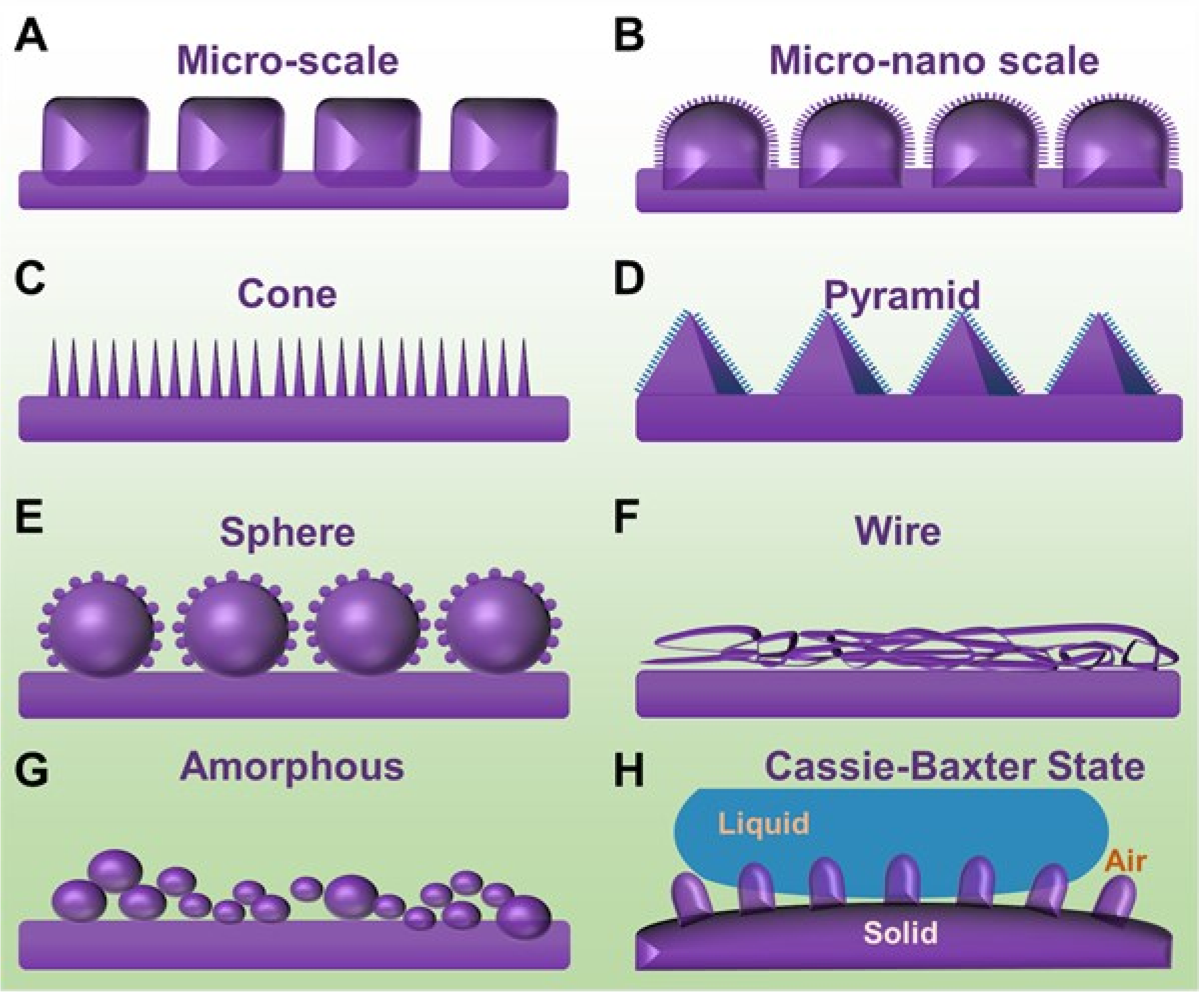

Figure 9. Modification of hydrophobic and hydrophilic properties of materials based on constructing nano-/microstructures. A) Microscale synapse model; B) Micro-/nanoscale synapse model; C) Microscale cone model； D) Micro-/nanoscale pyramid model; E) Micro-/nanoscale sphere model; F) Micro-wire model; G) Amorphous model; H) Cassie–Baxter state model.

In addition to these studies and modifications of the hydrophobicity of the material, there are a few studies on increasing the surface roughness of the material to improve its hydrophobicity. The corresponding classifications are shown in **Figure 9**. In 2020, Yu et al. reported a fibrous membrane based on PU, PAN, and fluor silane-modified silica nanoparticles (F–SiO_2).[137] The hydrophobic inorganic F–SiO_2 can improve the roughness and reduce the surface energy of the membrane, consequently improving the hydrophobicity of the nanofibrous membrane. The prepared hybrid porous membranes possess a robust tensile strength of 19.5 MPa, WVT of 10,300 g $(m^2{\cdot}d)^{-1}$, and a moderate WCA of 137.2°. In addition, the modification of the hydrophobicity of materials using silica-based particles was also studied. Gu et al. designed a hydrophobic and breathable PU/ hydrophobic silica gel fibrous membrane via electrospinning and post-heat treatment. Hydrophobic silica gel can significantly improve the mechanical properties, thermal stability, and waterproofness of composite membranes.[138] The obtained membrane exhibited a WCA of 142°, favorable hydrostatic pressure of 5.5 kPa, moderate WVT of 8,050 g $(m^2{\cdot}d)^{-1}$, and high air permeability of 9.3 $L/(m^2{\cdot}s)^{-1}$. Moreover, studies based on forming bead joints to adjust the hydrophobicity were conducted. In 2018, Jiang et al. reported a facile methodology to prepare ultra-hydrophobic fibrous membranes based on PVDF by high-humidity-induced electrospinning.[78] The special microsphere fiber increases the roughness of the membrane, subsequently improving the hydrophobicity. The optimized membrane showed a high WCA of 154°, a hydrostatic pressure of 62 kPa, and a WVT of 10,600 g $(m^2{\cdot}d)^{-1}$. However, as the fiber defect is caused by microspheres, the membrane exhibits unfavorable mechanical properties with a broken stress of 1.5 MPa. In addition, by designing this core–shell structure, a polymer with a low melting point can also be used for the shell material, and after heat treatment, moderate melting bonding can be formed between the fibers, which can significantly improve the mechanical properties of the prepared film.

Overall, the basic issues based on material designs and fiber structures are generally classified into two categories: 1) the design, selection, and adjustment of the hydrophilicity/hydrophobicity of materials; and 2) the construction of micro-/nanostructures on the electrospun fiber. Based on the resolution of these two basic issues, the protective film can strike a balance between moisture permeability, air permeability, and hydrostatic pressure resistance, thereby ensuring its comprehensive performance and further development of its functionalization.

4.2. Design of membranes with hierarchical layers

In addition to regulating the performance of the protective film with respect to material design and the surface structure of fiber, other studies have focused on the construction of multilayer protective membranes and functionalized protective membranes based on hierarchical layers. Most of these studies focused on the control and preparation of different layers of hydrophilic and hydrophobic membranes or the preparation of membranes with adjustable channel pore diameters to achieve a unidirectional moisture conduction or quick-drying functions.

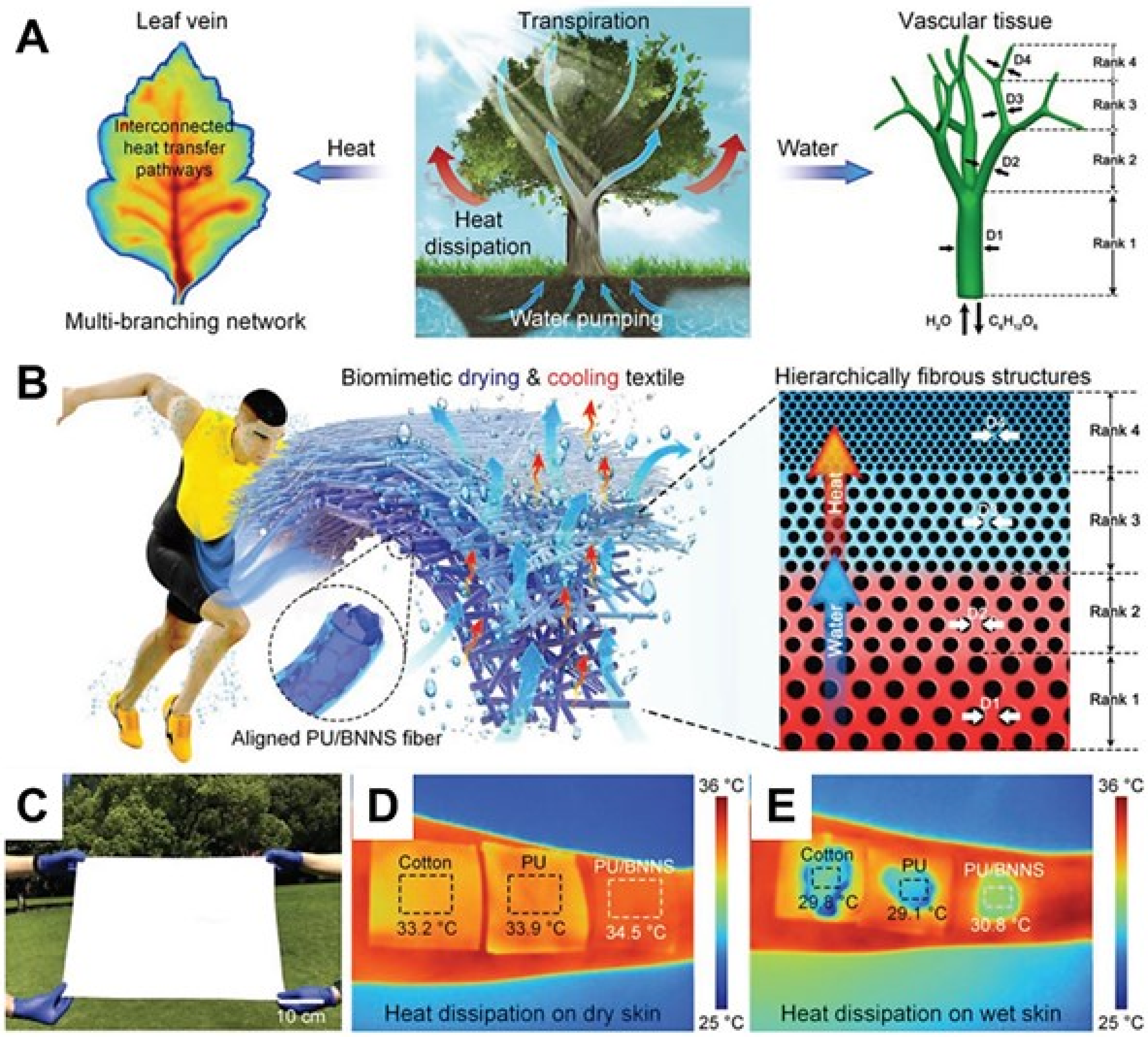

Figure 10. Multilayers of nanomembranes for quick-drying clothing. A) Transpiration process in plants. B) Sweat release and heat dissipation of the biomimetic multilayer fibrous membrane as a functional textile for personal drying and cooling. C) Photograph of large biomimetic multilayer fibrous membrane. D, E) Infrared thermal images of the heat dissipation performance of the cotton fabrics, PU multilayers, and PU/ boron nitride nanosheets (BNNS) multilayers in dry (D), and wet (E) state, respectively.[112] Reproduced with permission. Copyright 2021, John Wiley and Sons/Wiley-VCH.

To construct a typical moisture unidirectional transport membrane, at least two different hydrophilic and hydrophobic membranes are required. The inner membrane near the skin is usually hydrophobic, whereas the outer membrane in contact with air is usually hydrophilic. The hydrophobic film on the inner side provides a dry and comfortable feel to the wearer, while the outer film is a hydrophilic film that serves as a siphon and conducts water; it can achieve the spontaneous conduction of water from the inner to the outer side. The more significant the difference between the hydrophilic and hydrophobic properties of the two membranes, the more conducive is the construction of an efficient unidirectional water transportation membrane. In addition, considering that the siphoning effect is affected by the pore size, the pore size of the inner hydrophobic membrane is usually more prominent than that of the outer hydrophilic membrane. The small pore size of the outer hydrophilic membrane can effectively improve the siphoning effect and increase the efficiency of unidirectional wetting, as shown in **Figure 10**.

In scientific research and industry, the one-way water transport capability index, R, is generally used to characterize the unidirectional wetting effect of the film. The equipment used for evaluating the one-way water transport capacity is moisture management tester (MMT). The one-way transport capability is obtained by calculating the ratio of the integral difference of water conduction between the upper and lower sides of the membrane.[139] Generally, products with R > 1,000% are excellent unidirectional moisture-conducting products. Based on the design principle of the aforementioned one-way moisture-transport product, in 2017, Babar et al. reported a dual-layer surface-treated nonwoven/electrospun nanofiber membrane that possesses an excellent differential liquid moisture transport characteristic.[140] In the structure design, as the nonwoven fabric has excellent moisture release/absorbing features, it was used as the inner layer; because PAN is hydrophilic, it was used as an outer layer. The nonwoven layer was treated with polydopamine (pDA) to improve the wettability, and SiO_2 nanoparticles enhanced the hydrophilicity of the PAN layer. The optimized membrane possessed a high R value of 1,413% and an excellent OMMC of 0.99. The fabricated membrane can be used for quick-drying clothing. However, important parameters related to the hydrostatic pressure resistance of the membrane were not considered. Few subsequent studies have provided some improvements by comprehensively considering the performance of the protective membrane. In 2017, Ju et al. prepared a double-layer membrane containing a hydrophobic PU nanofiber membrane and a hydrophilic PU/ tetrabutylammonium chloride (TBAC) nanofiber membrane.[141] A small amount of TBAC can assist in obtaining a tree-like nanofiber structure. The formation of the tree-like structure can increase the critical surface area and make the membrane hydrophilic. This can improve the capillary effect to promote unidirectional moisture transportation. The fabricated membrane shows a tensile strength of 2.9 MPa, friction coefficient of 0.49, OMMC of 0.35, WVT of 2,170 g $(m^2 \cdot d)^{-1}$, and hydrostatic pressure of 10,000 mm H_2O. In 2018, Miao et al. reported a trilayered fibrous membrane for functional moisture transport.[95] In the design of the membrane, hydrolyzed PAN–SiO_2 was used as the outer layer to transfer the sweat out; hydrophobic PU was chosen as the inner layer to tune the anisotropic wettability; hydrolyzed PU–HPAN was selected as the transfer layer, which can guide the water transportation from the inner to the outer layer and prevent the inverse process. The trilayered hydrophobic fibrous membranes showed a high one- way transport index, R, of 1,021% and a favorable breakthrough pressure of 16.1 cm H_2O. The ultrahigh directional water transport capacity of the obtained membranes is valuable for personal quick-drying textiles.

Thus far, there remains significant room for research in balancing some of the comprehensive properties of the protective film, such as mechanical properties, hydrostatic pressure resistance, air permeability, and durability. It is worth mentioning that the interaction between the hydrophilic and hydrophobic layers has been neglected in several reports, so it is possible that the bonding between two or more layers of films with different hydrophilic and hydrophobic properties is not sufficiently strong. Therefore, it is easy to peel two or more layers, eventually leading to poor durability of the product. In addition, impurities and particles contained in the liquid are likely to block the pores of the fibrous membrane after long-term use, thereby affecting user experience.

4.3. Bionic design of fibrous membrane

With the development of bionic technology, significant progress has been achieved in various fields. Many researchers have attempted to use the knowledge gained from nature in the preparation of advanced functional products. Nanofiber products inspired by natural structures, such as lotus leaves, polar bear hair, and spider webs have been produced. It was observed that the leaves of lotus flowers have various secondary nanostructures, so they possess good water repellent and self-cleaning functions. The hair of polar bears has a typical hollow structure, so it has excellent thermal insulation; spider webs have high toughness, so that they can be used to capture insects. Numerous biological phenomena have attracted the attention of several researchers, and inspired by these phenomena, various electrospun products, as shown in **Figure 10**, have been designed.

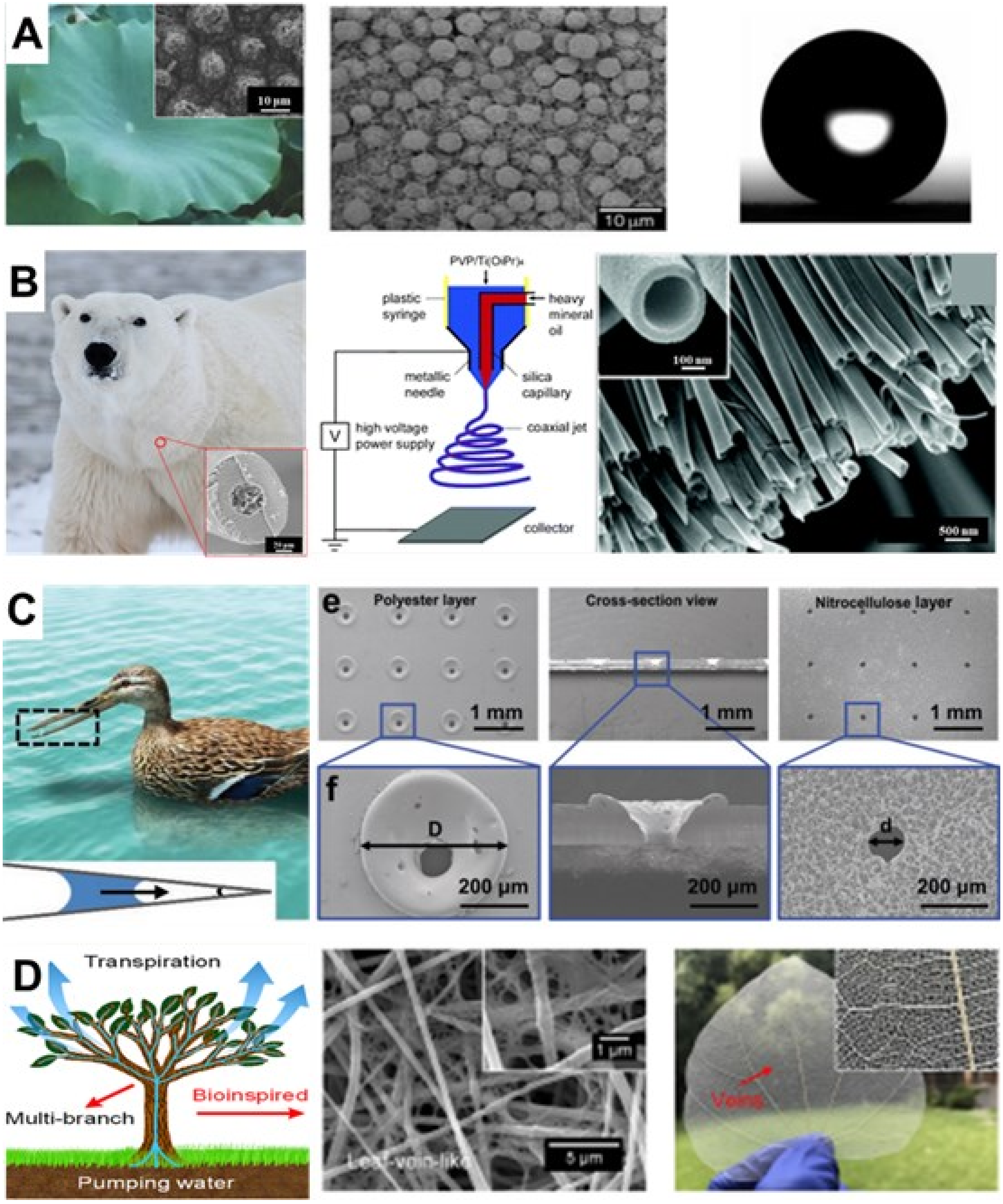

Figure 11. Various bionic designs of multifunctional membranes. A) Macro- and microscale images of lotus leaf, as well as the bionic lotus leaf structures with super-hydrophobicity prepared by electrospinning.[142] Reproduced with permission. Copyright 2004, John Wiley and Sons/Wiley-VCH. B) Hollow-structured bear hair and the hollow-structured nanofibers with thermal retention by coaxial electrospinning technology.[143] Reproduced with permission. Copyright 2004, American Chemical Society. C) Tapered duckbill structure and the electrospinning membrane with tapered structure for unidirectional water transport.[144] Reproduced with permission. Copyright 2019, John Wiley and Sons/Wiley-VCH. D) Plant

transpiration and constructed Murray membrane with ultrafast water transport and evaporation.**[145]** Reproduced with permission. Copyright 2018, American Chemical Society.

In nature, the lotus leaf effect is a typical example of increasing the hydrophobicity of a material by increasing its surface roughness. Microscopy revealed that the surface of the lotus leaf has several papillary structures in the micro/nanoscales, as shown in **Figure 11**. These structures significantly increase the surface roughness of the lotus leaf, so the gap between the water drop and the lotus leaf is filled with air. Therefore, the contact angle between the water droplet and the surface of the lotus leaf is a superhydrophobic angle higher than 150°. Inspiration from the physical structure of natural materials has tremendous significance for the future design of new material structures. When an electrospun dilute polymer solution can produce beads-on-string fibers, artificial surfaces with the characteristics of lotus leaves can be achieved. Prof. Lei Jiang first prepared a superhydrophobic electrospun film containing beads/fibers using a dilute polystyrene (PS) solution.[142] The prepared porous beads were 3–7 μm in size, and the fiber diameter was 60–140 nm. The prepared film possessed excellent super-hydrophobicity, and its WCA can reach 160°. This study successfully simulated the leaf structure of lotus, which has great significance for subsequent bionic structure research. However, the mechanical properties and other comprehensive properties of the membranes were not reported in this study. Subsequently, Acatay et al. revealed a superhydrophobic bionic lotus leaf film via poly(acrylonitrile-co-a,a-dimethyl meta-isopropenyl benzyl isocyanate) -based electrospinning. In this study, the authors increased the WCA to 167°. [146] Recently, Jiang et al. reported a facile method to prepare PVDF-based ultra-hydrophobic fibrous membranes under high humidity conditions by electrospinning. The special microsphere-fiber increases the roughness of the membrane to improve its hydrophobicity. The optimized membrane showed a high WCA of 154°, hydrostatic pressure of 62 kPa, and WVT of 10,600 g $(m^2\cdot d)^{-1}$. However, as the fiber defect is caused by the microsphere, the membrane has unfavorable mechanical properties with a broken stress of 1.5 MPa.

The polar bear is an animal that lives in extremely cold regions. During long-term biological evolution, a special structure of hair with a hollow core was developed. The hair of polar bears is filled with air with low thermal conductivity, significantly improving its thermal insulation properties, thereby playing a crucial role in keeping them warm. The structure of polar bear hair, with multi-channel microtubes is shown in **Figure 11**. Inspired by this structure, researchers have designed hollow nanofibers by electrospinning. In 2006, Prof. Lei Jiang's group used paraffin oil and $Ti(OiPr)_4$ solution to prepare various fibers with complex hollow structures through multi-fluidic compound-jet electrospinning technology.[147] Electrospun nanofibers with two–five hole structures were fabricated through the modification of channels in the needle of electrospinning. However, the coaxial electrospinning has many drawbacks. Related quantitative studies have shown that for the preparation of the stable core-shell electrospun fiber, a series of spinning parameters need to be precisely designed, such as the ratio of the viscosities of core and shell solutions, the structure of nozzles, and the electric field intensity. By adding surfactants, the ratio of the viscosities of core and shell solutions can be adjusted greater than a threshold for obtaining the stable coaxial Taylor cone and the uniform core-shell fiber.[148] Xin Wang et al. quantitatively studied the impact of different nozzle structures, concave type, flush type, and convex type on the spinnability of core-shell fibers. Authors found that the nozzle with concave structure benefits the uniformity of the electric field intensity distribution, and the stable coaxial electrospinning.[149] In 2018, Saeedeh R. et al. confirmed this view, meaning that the core and shell diameter of the fiber are dramatically impacted by nozzle diameter and polymer solution concentration.[150] So, the control, optimization, and stability of the coaxial electrospinning is a serious concern, especially in the process of industrialization. According to the principle of heat conduction, the prepared hollow fibers should exhibit a favorable thermal insulation effect. Subsequent studies continued the preparation of porous nanofibers by blending two-phase incompatible polymers for electrospinning or using two or more solvents with different volatilities to prepare microporous nanofibers. Miyauchi et al. reported a method for preparing porous PS electrospun fibers using a mixed solvent of THF and DMF.[151] During electrospinning, owing to the different volatilities of the two solvents, the PS phase separates, so the obtained fiber has numerous fine microporous structures, and its contact angle can reach 160°. There have been several related studies on porous nanofibers. However, it is worth mentioning that most of the studies only focused on the characterization of the fiber and its microscopic morphology, and few studies focused on the comprehensive properties of the prepared porous fibers and their membranes. Therefore, in the future, based on the current research on morphology design, more attention should be paid to the comprehensive performance of nanoporous products, which is beneficial for promoting the practical applications of bionic porous nanofibers.

In addition, a few studies have designed electrospun fibers or films based on the bionic simulation of the transpiration of spider silk, duckbill, and the structure of plants to realize specific applications. Based on the unique process of spider silk spinning, Liu Y et al. developed an electrospinning technology known as bubble electrospinning that involves the ejection of polymer jets from the bubbles formed by a highly charged-aerated polymer solution.[152] Based on the excellent wettability of duckbills, in 2019, Bing Dai reported a bioinspired Janus textile with conical micropores for human body moisture and thermal management.[144] The research involved the fabrication of a multilayer Janus membrane with hydrophobic polyester and super-hydrophilic nitrocellulose embedded with a conical micropore array on the inner surface. The obtained membrane showed an excellent directional liquid transport with a directional water transport capability of 1,246%. The membrane possessed a thermal retention property, maintaining a human body temperature 2–3 °C higher than that maintained by cotton textiles. The mechanism of directional water transmission was also developed, demonstrating that the hydrophobic polyester layer with the larger opening of micropores to water, and the multilayer membrane can easily pump water to the hydrophilic layer. In addition, the designed Janus membrane is comparable to traditional products with respect to other properties such as water wicking and air permeability. Inspired by the structure of plant fibers and plant transpiration, researchers have prepared advanced fast-drying fabrics by designing multilayer film structures. In 2019, inspired by the transpiration process in vascular plants, Wang et al. fabricated a series of Murray networks via electrospinning.[145] The obtained electrospinning web simultaneously exhibited anti-gravity directional water transport and ultrafast evaporation. The prepared Murray membranes showed an R value of up to 1,245%, an OMMC of 0.94, and a moderate water evaporation rate of 0.67 g h^{-1}. In addition, in an article based on Murray's law, the mechanism of the multi-branching porous structure and surface energy gradient was well disclosed. The fabricated biomimetic porous Murray nanofibers are promising for application in moisture-wicking technologies for personal comfort management. The anti-gravity water transportation in plants is of great significance for water conduction and transportation. There is great potential for the development of construction methods for bionic fiber structures. It is considered that more high-performance membranes will be developed for daily use based on bionic technology in the future.

5. Various applications of fibrous membrane

Electrospinning has good operability, and can be easily employed to prepare micro/nanostructured fibers. The prepared samples have large specific surface areas. Therefore, electrospinning technology has broad applications in biomedicine, filter materials, and protective clothing. Electrospun protective membranes have various uses that combine waterproofing, breathability, moisture management, and thermal regulation. With the development of electrospinning technology, high-efficiency needleless electrospinning technology and its unique fiber structure are predicted to promote developments in intelligent manufacturing, wearable electronics, industry 4.0, and so forth.

5.1. Waterproof and breathable membranes

Breathable membrane materials are functional polymer materials with good market prospects and increasing demands. It allows the selective permeation of water vapor and water droplets, that is, it prevents liquid water from permeating while facilitating the permeation of water vapor. The permeation of water vapor is of great significance for the thermal management of the human body.[102] During high-intensity exercise, the permeation of water vapor can effectively reduce the high temperature of the body surface and improve the comfort of the wearer. Similarly, in a cold environment, such as snowy mountains, a low water vapor permeation rate can cause frostbite or death to the wearers owing to the condensation of water vapor underneath the clothing. Therefore, water vapor-permeable and waterproof clothing have a wide range of applications in outdoor clothing, medical and health field, precision electronics, and building materials, as shown in **Figure 12**.

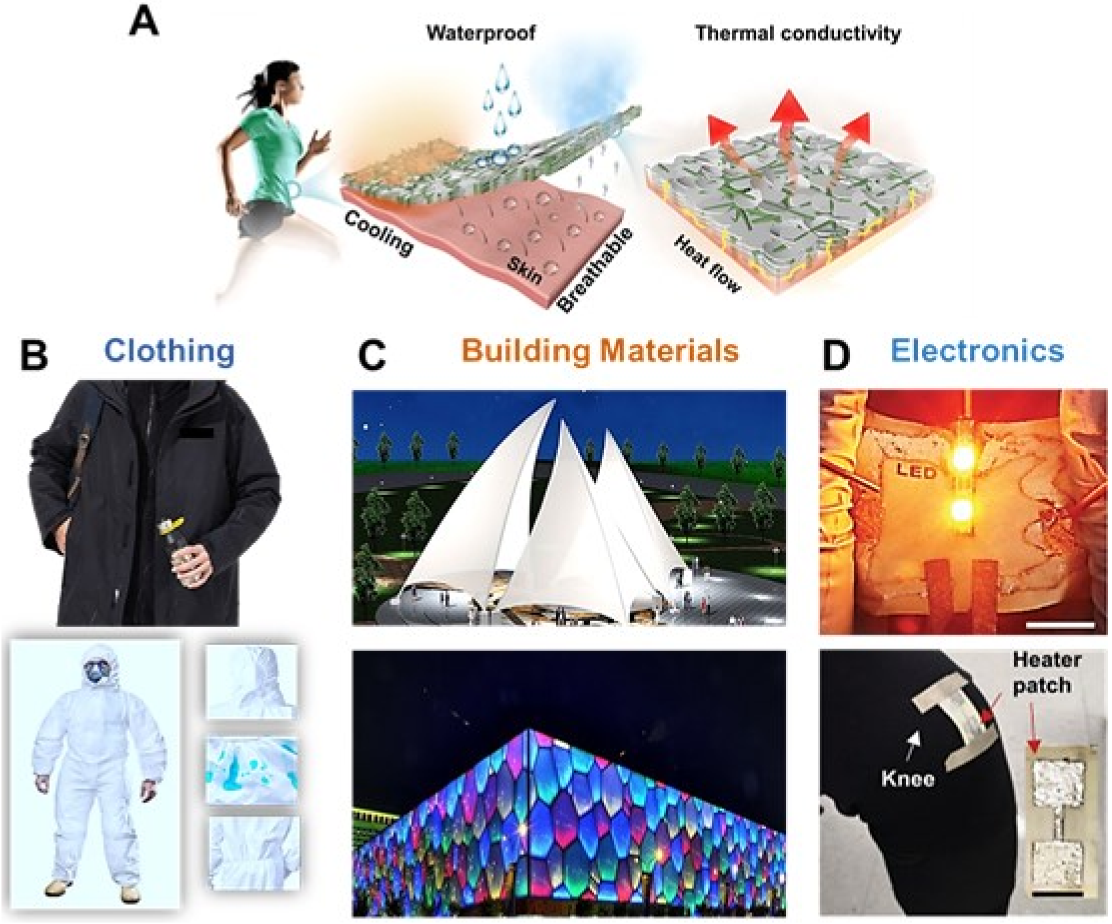

Figure 12. Diverse applications of waterproof and breathable membrane. A) Schematic of waterproof and breathable membrane.[153] Reproduced with permission. Copyright 2020, American Chemical Society. B) Application of waterproof and moisture-permeable membrane in jackets and medical protective clothing. C) Application of waterproof and

moisture-permeable membrane in building curtain wall. D) Optical images of patterned Liquid metal-lyophilic Ag-SBS (LA-LAg-SBS) as the stretchable electrical circuit and sensor.**[154]** Reproduced with permission. Copyright 2021, John Wiley and Sons/Wiley-VCH.

According to the principle and structure of the waterproof and breathable membranes, they are mainly divided into two categories: 1) porous structure-based waterproof and breathable membranes, and 2) non-porous, waterproof, and breathable membranes. Among them, porous structures refer to membranes that usually contains pores with sizes of 0.5–20 μm and owing to the function of these micro/nanopores, the membranes exhibit waterproof and water vapor-permeable functions.[130] E-PTFE film is a representative of this type of film, but there are a few limitations for products of this type: 1) during manufacturing, heating is required, leading to high energy costs; 2) preparation processes are complicated, resulting in high equipment cost; 3) PTFE is not easily degradable, consequently causing environmental pollution.[155]

Nonporous waterproof and moisture-permeable membranes are usually hydrophilic membranes. This membrane possesses a stable WVT, that is, the WVT would not reduce owing to micropore clogging during usage.[119] Typical films of this type are hydrophilic polyester and PU films. Introducing hydrophilic groups, such as amino, hydroxyl, ether, and carboxyl groups, can improve the hydrophilicity of the molecular chain to achieve moisture permeability of the membranes.[11] The principle of breathability of hydrophilic membranes is the adsorption–diffusion–desorption process. Owing to this moisture permeability principle, it is difficult to achieve high moisture permeability in non-porous waterproof water vapor permeable membranes. In addition, the molecular structure design of traditional hydrophilic membranes is complicated, the synthesis is challenging, and the mechanical properties of the prepared products are insufficient. These factors limit the use and industrialization of non-porous, waterproof, and moisture-permeable membranes. Therefore, it is important to develop new technologies for high-performance, waterproof, and breathable membranes.

Table 2. Performances of waterproof and breathable membrane reported in recent years.

Materials	Additives	WVT/ (g/m^2·d)	Broken Stress (MPa)	Hydrostatic Pressure (kPa)	Air Permeability (mm/s)	Ref.
PVDF	-	10,870	40	102	-	[156]
PVDF	-	10,600	1.5	62	1.3	[78]
PVDF	F-TiO_2	10,600	15.1	60.2	-	[116]
PVDF	$AgNO_3$	2,915	23.4	-	-	[157]
PVDF/PVB	-	10,600	10.5	58	9.8	[82]
PVDF/PVB	CNTs	7,846	20.2	59.2	-	[158]
PVDF/PVA/PAA	-	12,600	-	70	-	[159]
PU	SiO_2	7,290	-	13	-	[160]
PU	-	4,200	-	75	4	[161]
PU	TiO_2/FAC	12,900	14.6	62	-	[162]
PU	SiO_2	8,050	-	5.5	-	[138]
PU	SiO_2	10,400	42	50	-	[163]
PU	-	19,300	12.1	2.8	962	[164]
PU	F-SiO_2	9,060	10.4	12.6	4.8	[165]
FPU	TTMA^4	13,100	8.5	86.2	5.5	[166]
FPU	BNs^5	11600	32	-	-	[153]
PU/FPU	CNTs	9,200	12.5	108	-	[94]
PU/FPU	$AgNO_3$	12,900	9.8	102.8	-	[167]
PU/FPU	-	11,900	10	86	-	[135]

PU/FPU	$MgCl_2$	11,500	12.4	104	-	[92]
PU/Nylon66	-	1,280	-	-	10	[168]
PU/PMHS[1]	-	9,500	14	54	-	[169]
PU/PVDF	-	11,300	13	140	-	[170]
PU/PCL[2]	-	9,030	12	73.6	-	[171]
PU/FPU	-	11,800	11.4	88.2	-	[172]
PU/PVB/BIP	-	9,600	33	110	-	[110]
PU/PAN	F-SiO_2	10,300	19.5	-	-	[137]
PAN	SiO_2	11,400	-	74.3	20.5	[173]
PAN/PDMS	-	12,500	15.7	80.9	9.9	[136]
PAN/FPU	-	10,100	9.4	114.6	-	[174]
PAN/FPU	-	9,200	20	83.4	-	[109]
PDMS/PVB	-	8,980	5	54	-	[175]
SBS	-	4,540	-	63.9	5.69	[120]
m- aramid	LiCl	7,650	-	-	-	[176]
PAMPS[3]	GO[6]	1,450	4.5	-	-	[177]
Polyamide	-	11,200	15.6	101.2	2.6	[127]
Polyamide	-	10,300	-	106	-	[178]

1: polymethylhydrosiloxane; 2: poly (ε-caprolactone); 3: poly(2-acrylamido-2-methyl-1-propane sulfonic acid); 4: tris(2-methyl-1-aziridinepropionate); 5: boron nitride; 6: graphene oxide.

In recent years, the reliance on advanced electrospinning technology, waterproofing, and moisture-permeable nanomembranes has been increasing rapidly. In 2002, Chang Seoul first reported that electrospinning can be used for the research of waterproof and moisture-permeable smart clothing.[81] Furthermore, this technology has been developed based on advanced materials such as PVDF, PAN, PU, and advanced equipment, such as core–shell structures, hybrid co-spinning, single needle/multi-needle, and needleless technology. The membrane exhibited improved the overall performance including moisture permeability, mechanical strength, and hydrostatic pressure resistance.

Among listed investigations, the representative technology reported by Junlu Sheng in 2016, who developed a chemical modification method to enhance the mechanical properties of fibrous membranes and maintain the waterproofness and breathability at a high level.[110] In this study, PU, PAN, and PVB were used for electrospinning, and BIP was added as the cross-linker. After the heating post-treatment, the overall performance of the composite membrane significantly improved. The obtained membrane showed a high tensile strength of 33 MPa and a high WVT of up to 9,600 g $(m^2 \cdot d)^{-1}$. This intriguing method provides a valuable platform for bonding fibers and enhancing the properties of the membrane. Compared with studies on traditional waterproof and moisture-permeable products, this study provides a promising approach for constructing nanofibrous membranes. Interestingly, Yue et al. constructed a thymol-loaded PU fibrous membranes with waterproof, breathable, and antibacterial properties, which have the potential for wound dressing applications using portable electrospinning devices.[179] In addition, based on the improvement of the key elements, such as breathability, mechanical properties, and hydrostatic pressure of waterproof and breathable membranes, recent research results are summarized in Table 2. At present, we know that the highest achievable mechanical strength is 42 MPa; the maximum achievable WVT of the membrane is 19,300 g $(m^2 \cdot d)^{-1}$; the maximum achievable hydrostatic pressure is 115 kPa. On comparing the properties of the materials studied in current research, mainstream products, such as Gore-Tex, may face substantial competitive pressure in the future.

Notably, there are various types of tests for waterproof and water moisture permeability, such as determining the hydrostatic pressure and WVT, which differ significantly between the American and Japanese standards. Considering the development of moisture-permeable films, it is essential to combine these testing methods. Currently, it is expected that the moisture permeability of products can be evaluated using an efficient and accurate sweating dummy. In addition, with the development of material science and the innovation of electronic technology, it is expected that waterproof and water-moisture-permeable membranes are applied in these products. Flexible electronic skin is significant for the development of breathable membranes in the future. To realize this application, researchers require to focus on improving biological and electronic technical indicators, such as biocompatibility, specific immune response, and electrical conductivity, based on the comprehensive performance of hydrostatic pressure resistance and moisture permeability.

5.2. Unidirectional water-transport protective membrane

The water moisture transmission of the fabric is an essential factor that affects clothing comfort. Suppose that the sweat secreted by the human body is not quickly transferred to the outer surface of the fabric. In this case, it will cause significant discomfort for wearers, consequently leading to the formation of breeding grounds for bacteria and is a potential health hazard to the wearer. The unidirectional water transmission membrane exhibits directional transmission of water molecules owing to its different hydrophilic and hydrophobic abilities on both sides of the surface. Some people refer to this functional membrane as a humidity diode. The unidirectional water transmission membrane can transport sweat and water vapor from the body to the external environment, providing the human body with a rapid drying and comfortable micro-environment. With the rapid development of high-end sportswear, field uniforms, diapers, wound dressings, and other advanced clothing, the demand for unidirectional water transmission and quick-drying membranes has increased. Representative research and its applications are shown in **Figure 13**.

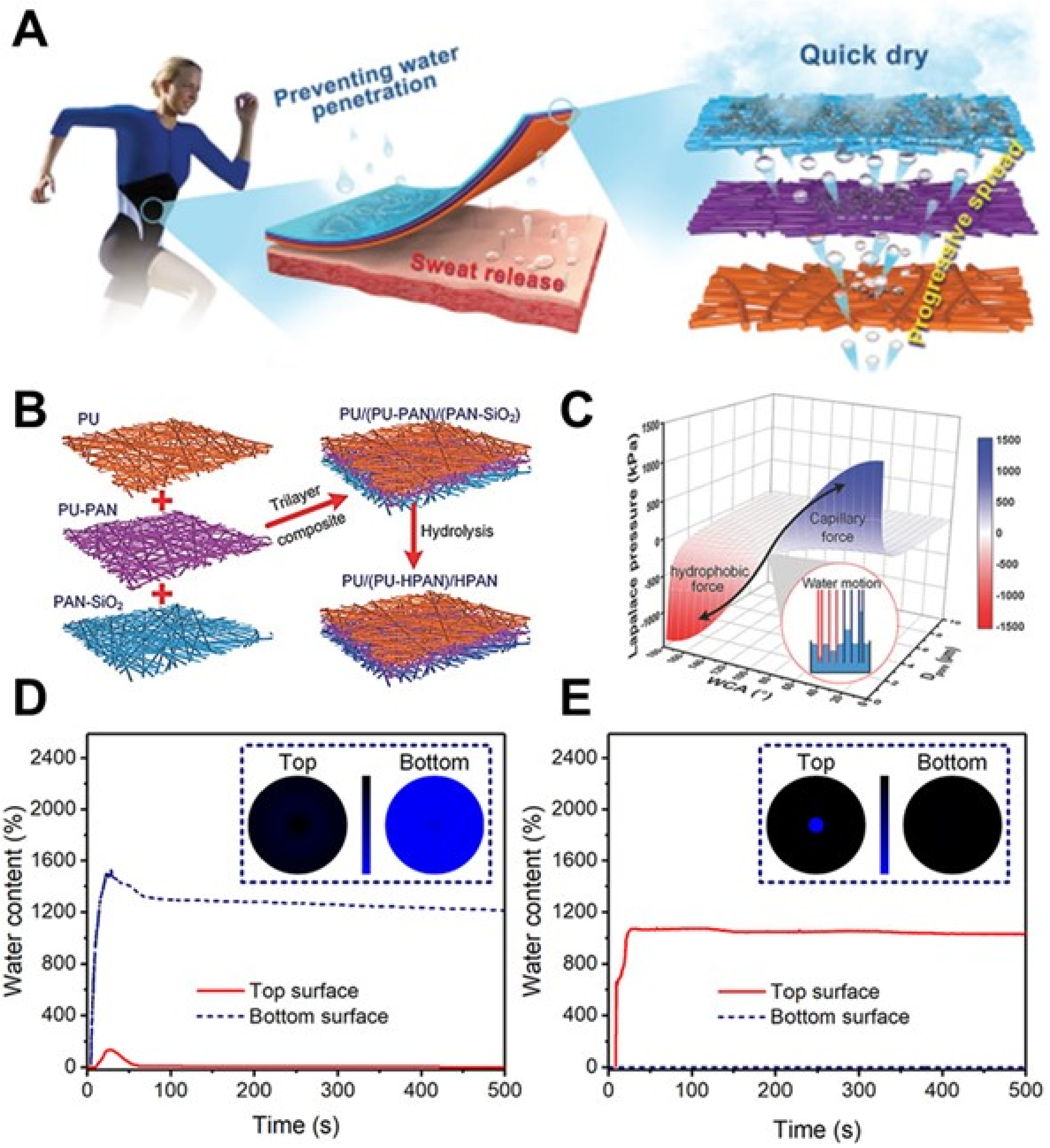

Figure 13. Representative application of one-way transmission membrane. A) Sweat release process of the functional moisture wicking textiles. B) Fabrication of trilayered PU/(PU–HPAN)/HPAN fibrous membranes. C) Laplace pressure versus WCA and pore diameter of

the fibrous membrane (D_{pore}), which provides two opposite forces to drive the water motion in the inter-fiber capillary channels.**[95]** Reproduced with permission. Copyright 2018, John Wiley and Sons/Wiley-VCH. (D, E) MMT results of the porous Murray membranes with C6FPU loading weights: (D) 0.6 and (E) 3 g m^{-1}.**[145]** Reproduced with permission. Copyright 2018, American Chemical Society.

Based on the different principles of unidirectional water transmission, they can be roughly classified into three categories. The first is the differential capillary effect, in which researchers use the capillary effect to achieve unidirectional water transmission. It increases the wicking performance and transmission rate by gradually narrowing the capillary diameter from the bottom to top.[180] In the double-layer fabric structure, including thinner and thicker capillaries from the outer and inner fibers, respectively, of the fabric, a significant difference in wicking force occurs between the inner and outer interfaces of the fabric. The liquid water in the fabric is transferred under the action of this pressure difference. It transfers from the inner layer to the outer layer, forming a unidirectional water transmission phenomenon. The second category is the wetting gradient effect. In nature, beetles and spiders have an excellent water collection ability because of the difference in surface wettability.[181] The hydrophobic area on the surface collects water from the air and is gradually transported to the hydrophilic area. According to this principle, when the fabric has a hydrophilic/hydrophobic two-layer structure, it produces a wetting gradient, achieving efficient unidirectional water transmission. The third category is transpiration. This phenomenon is observed in plant transpiration, where gravity is overcome to absorb water from the soil, transport it to the leaves through the xylem, and then removes water from the stomata and evaporates.[182] The transport efficiency of water vapor produced by this phenomenon is significantly greater than the evaporation rate of water molecules on the free surface. The simulation of this multilevel bionic structure can enable the preparation of highly efficient unidirectional water transmission products.

Fiber products with a high specific surface area can be prepared using advanced electrospinning technology. The increase in specific surface area can promote the rapid conduction and evaporation of water molecules. Then, through a special structural design, excellent unidirectional water transmission products can be prepared. A one-way wet-conducting film based on electrospinning technology was first reported in 2017 by Aijaz Ahmed Babar, who constructed a dual-layer surface-treated nonwoven/electrospun nanofiber membrane based on PAN that exhibited excellent differential liquid moisture transport characteristics.[111] The nonwoven layer was treated with pDA to improve the wettability, and SiO_2 nanoparticles enhanced the hydrophobicity of the PAN layer. The optimized membrane possesses a high one-way transport capacity of up to 1,413% and an excellent OMMC of 0.99. Based on this research, porous electrospinning membranes were constructed. The PVP was blended and washed from the fiber matrix of PAN to obtain a high roughness and porous PAN for the first layer. The second layer was subsequently fabricated using PU nanofibers via electrospinning. The resultant Janus membrane possessed a one-way water transmission property with an R value of 1,311% and a breakthrough pressure of 17.1 cm H_2O.[107] At present, the highest achievable R value is 1,413%, as listed in Table 3. In addition, researchers tend to combine waterproofing and one-way transmission based on the construction of multifunctional one-way water transmission products. The challenge is the construction of products with high R and high hydrostatic pressure resistance. Compared with commercial waterproofing and breathable products, hydrostatic pressure resistance has significant potential for improvement.

Table 3. Performance of one-way water transport membrane via electrospinning.

Materials	Additives	R	OMMC	WVT/(g/m^2•h)	Ref.
PU	TBAC	34.9	-	2,170	[141]
PU/BNs	-	1,072	-	-	[112]
PU/PAN	SiO_2	1,021	-	-	[95]
PAN	SiO_2	1,413	0.99	12,730	[111]

PAN/PU	-	1,311	-	-	[107]
PLA/Cellulose	-	1,245	0.94	-	[145]
CA	-	919	0.89	12,110	[183]
Polyamide	Ag	1,253	0.91	11,450	[140]

The transpiration phenomenon observed in plants has two characteristics: self-driven anti-gravity directional water transport and ultra-fast evaporation. Wang et al. utilized synthetic materials and fabricated a series of Murray networks via electrospinning inspired by the transpiration process in vascular plants.[145] The obtained electrospinning web simultaneously realized anti-gravity directional water transport and ultrafast evaporation. In addition, in an article on Murray's law, the mechanism of the multi-branching porous structure and surface energy gradient was reported. The fabricated biomimetic porous Murray nanofibers have promising applications in moisture-wicking technologies for personal comfort management.

In addition, a few studies have not evaluated the mechanical strength and other comprehensive properties of unidirectionally wetted membranes. Another limitation is that the interforce between the two layers is not adequately strong in principle because of the significant differences in the molecular chain structures between the hydrophilic and hydrophobic membranes. Therefore, enhancing the interaction force between the hydrophobic and hydrophilic membranes is essential to enable the practical application of directional water transmission membranes. In the future, with the development of smart clothing, biomedicine, and flexible microelectronics, directional water-absorbing and quick-drying protective fabrics potentially have great significance in various fields.

5.3. Other applications

Electrospun protective membranes have extensive applications, including waterproofing, moisture-permeable membranes, and unidirectional moisture transmission membranes. It has also been widely researched in various fields such as electromagnetic shielding, anti-ultraviolet radiation, functional antibacterial, and personal thermal management. Related research usually combines functional materials with an electrospun matrix to endow the as-prepared membranes with specific functionality to satisfy the application of fibrous membranes under the required conditions.

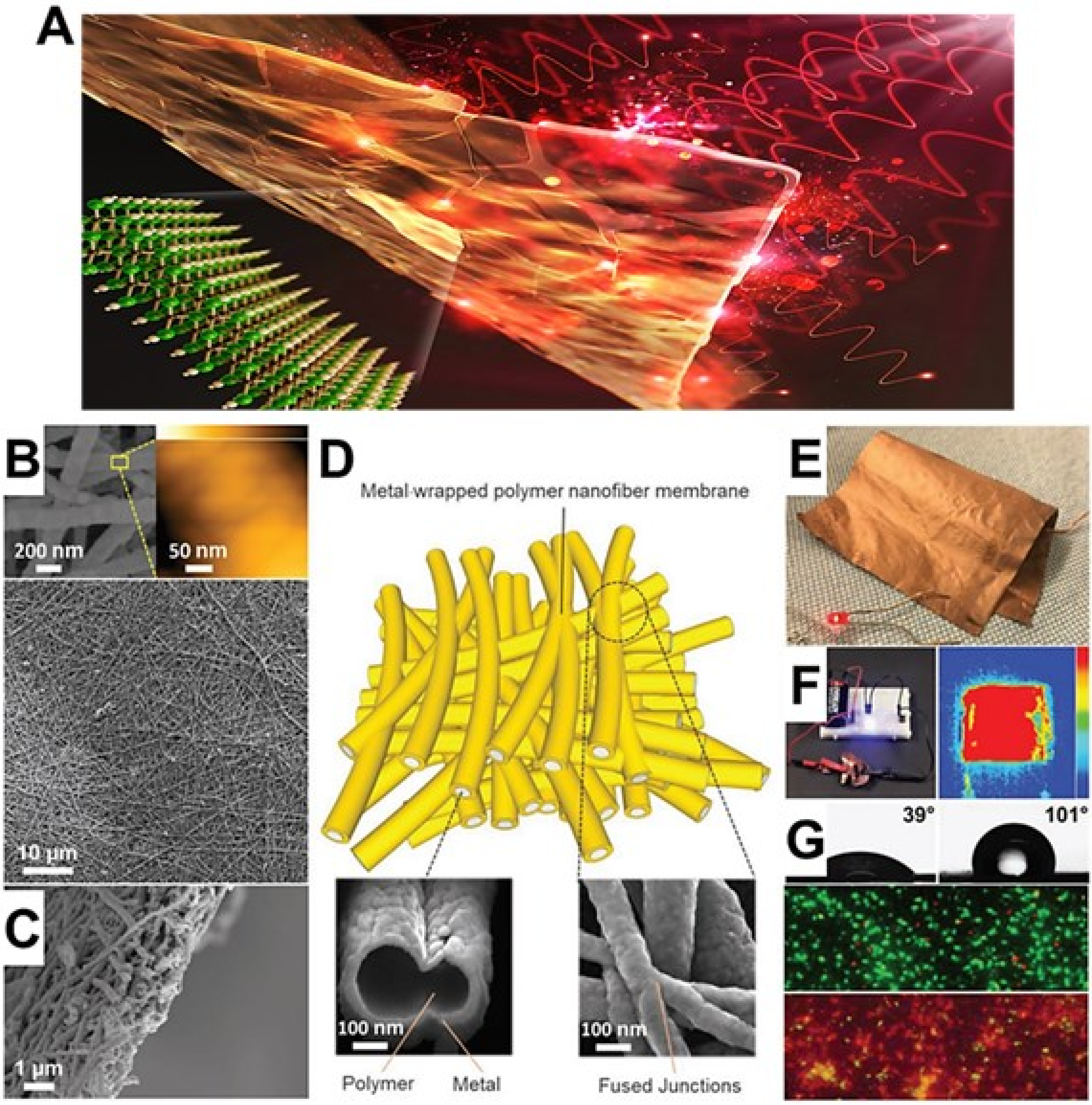

Figure 14. Fibrous membrane used for electromagnetic interference shielding. A) Schematic of electromagnetic shielding.[184] Reproduced with permission Reproduced with permission.

Copyright 2020, John Wiley and Sons/Wiley-VCH; B) SEM and atomic force microscopy images of the Cu-wrapped nanofibers in the cellular membranes; C) cross-sectional SEM image of the membranes; D) schematic and microstructure of the cellular membranes composed of high-conjunction Cu-wrapped polymer nanofibers; E) photograph of a large-area, flexible, and conductive membrane; F) continuous LED illumination regardless of highly wrinkled membranes; uniform electrothermal behavior of the membranes at a low driven voltage; G) contact angles of the cellular membranes without and with Cu layer; typical antibacterial performance of pure polymer nanofiber membranes and Cu-wrapped polymer nanofiber membranes.**[185]** Reproduced with permission. Copyright 2020, John Wiley and Sons/Wiley-VCH.

Electromagnetic radiation has been attracting increasing attention owing to the widespread use of electronic devices. This type of radiation emitted by devices such as mobile phones, computers, and televisions significantly affects human health. Electromagnetic radiation can be classified according to frequency from low to high, including radio waves, microwaves, megahertz radiation, infrared rays, visible light, ultraviolet radiation, X-rays, and gamma rays.[186] In principle, conductive metal materials generally exhibit favorable radiation shielding characteristics, and some nanomaterials, such as graphene, CNTs, and MXenes, also exhibit favorable electromagnetic shielding functions.[187] In 2020, Zeng et al. reported an ultrathin fibrous membrane with high electromagnetic interference shielding properties, breathability, antibacterial properties, and waterproofing properties.[185] These membranes were fabricated by pDA-assisted metal deposition technology, which can assist for metal particles well adhering on the electrospinning polymer nanofibers. The resulting fiber exhibits a metal-wrapped shell and polymer fiber-based core structure. Electromagnetic interference shielding effectiveness (SE) of the membrane can reach 53 dB at a low membrane thickness of 2.5 μm and a SE of 44.7 dB at the lowest thickness of 1.2 μm. In addition, the normalized specific SE reaches 232,860 $dB \cdot cm^2 g^{-1}$, which is higher than those of other reported shielding materials. This development potentially has various applications, such as wearable smart electronics for resisting electromagnetic radiation pollution, as shown in **Figure 14**.

In addition, UV-resistant materials are also a hot topic for research. Regardless of the traditional textile field and the emerging smart textile field based on electrospinning technology, preventing UV penetration, and ensuring wearing comfort are important issues. Therefore, research on anti-UV materials is of long-term significance.[188] UV is an electromagnetic wave with a wavelength between 10 and 400 nm. The wavelength is shorter than that of visible light, but longer than that of X-rays. UVA-1 has the highest penetrating power, and can reach the dermis and tan the skin. In 2020, Liu et al. reported a facile fabrication method for environmentally friendly, waterproof, and breathable nanofibrous membranes with suitable UV-resistant properties.[116] A hydrophobic agent and 2-hydroxy-4-methoxybenzophenone (UV9), fluorinated nano-titanium dioxide (F-TiO_2), was blended into the PVDF solution. The addition of F-TiO_2 NPs improved the waterproofing property of the PVDF membrane, while the synergistic effect between the inorganic particle, F-TiO_2, and organic UV absorber UV9 further significantly enhanced the UV resistance of the PVDF membrane. The optimized membrane showed a favorable WVT of 10,600 kg $(m^2{\cdot}d)^{-1}$, hydrostatic pressure resistance of 60.2 kPa, and high ultraviolet protection factor value of 1,690. Methods to reduce the amount of addition to improve the anti-UV efficiency significantly is the current focus of research in the development of anti-UV protective membranes

Finally, other studies have focused on endowing traditional waterproof and moisture-permeable electrospun membranes with antibacterial properties and thermal management functions by adding antibacterial agents, thermally conductive fillers, and phase change substances, such as silver nanoparticles, titanium dioxide, and quaternary ammonium salts. In 2018, Zhao et al. prepared a human skin-like breathable fibrous membrane with robust waterproof properties and antibacterial properties based on a novel type of PU elastomer.[167] In addition, $AgNO_3$ was added to enhance its comprehensive performance. The optimized PU/C_4FPU/$AgNO_3$ fibrous membranes showed excellent waterproofing properties. The membrane possessed significant antibacterial efficacy against Escherichia coli and Staphylococcus aureus. Moreover, in 2021, Miao et al. reported a biomimetic transpiration textile for highly efficient personal drying and cooling by mimicking the hierarchical and interconnected network of vascular plants.[112] In this study, hierarchically porous structures were constructed using PU/boron nitride nanosheets. The obtained membrane shows a high one- way water transport index of 1,072%, and an excellent thermal conductivities of 1.14 W $(m\cdot K)^{-1}$. The unidirectional water transport and excellent heat management of this smart membrane could provide a comfortable microclimate for the human body for next generation of smart textiles.

In addition to research on protective films, an increasing number of studies have used electrospinning technology to construct special structures to obtain functional application films for electronic skin, mechanical sensors, heavy metal adsorption, and smart photocatalysis. With the development of advanced materials, electrospun protective films are being increasingly used in diverse fields.

6. Conclusions and Future Perspectives

Electrospinning technology has been rapidly developing in the last two decades and has been applied in various fields such as biomedical sciences, integrated manufacturing, flexible electronics, and high-efficiency catalysis. It has been 20 years since electrospinning was used for protective clothing applications; in these years, electrospinning technology based on new materials, functional structures, and functional design has progressed significantly with respect to applications in smart clothing. Currently, additional to satisfying the market demand, the protective membranes with basic functions, such as waterproofing or medical protection, also pursues multi-functional membranes equipped with anti-UV, antibacterial, and wearable energy properties. Therefore, the demand for functional products is showing a significant growth trend.

At present, researchers have performed electrospinning research on over 100 types of natural/synthetic compounds, including PVDF, PAN, and PLA; considering the structural design, core–shell, side-by-side, hierarchical, and fantastic bionic structures have been realized via electrospinning technology; considering various applications such as breathable–waterproof, quick-drying protection, and special functional protective membranes have been fabricated and applied. Additional to the development of technology, corresponding material optimization and selection used electrospinning is gradually changing from traditional non-degradable, fluorine-containing materials to degradable materials, which can be metabolized by the environment; based on bionic structure design, researchers have investigated lotus leaves, hollow hair of polar bears, and plant structures, and numerous issues regarding the construction principles for super-hydrophobicity, efficient heat preservation, and anti-gravity water transportation have been solved; based on the functional design of the protective film, combined with advanced nanotechnology, using materials such as superhydrophobic silica, titanium dioxide, and CNTs, researchers have realized a series of functions, such as thermal management, antibacterial, anti-UV, and anti-electromagnetic waves. Protective films have been receiving increasing attention owing to the development of new materials and functional structures with diverse applications.

However, few limitations regarding electrospinning technology remain that are yet to receive sufficient attention. The development of materials and electrospinning technology, that is, green material design, environment-friendly processing, and efficient production during the industrialization of electrospinning are future development trends. Research based on high-concentration and green solvent electrospinning solutions is lacking; based on issues regarding the layered structures of electrospun fibers, more research on the methods to improve the efficient combination of the hydrophilic layer and the hydrophobic layer via physical, chemical, or corresponding post-processing technology is required; based on the properties of electrospun nanofibers, there is no report on the physical and chemical properties of spun monofilaments. More research on the electrospinning solution and the modification of the properties of monofilaments can provide an excellent foundation for the development of electrospinning technology for protective films.

In summary, in the past 20 years, electrospinning technology with respect to materials, structures, and multifunctionalities has been well developed. The achieved multifunctional protective membranes have been used in various applications such as personal protection, high-end sports, and special-operations uniform. However, research based on green processing, hierarchical design, and monofilament performance has rarely been reported. We are convinced that through the development of new materials, the improvement of post-biomimetic technology, and the advancement of cutting-edge detection technologies, these existing issues of electrospinning technology will be overcome one by one. In the future, the development of high-performance and multifunctional electrospinning protective films can significantly contribute to fields of electronic skin, smart wearables, high-end biomedicine, and future integrated manufacturing.

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Conflict of Interest

The authors declare no conflict of interest.

Reference

[1] K. Forsberg, A. Van den Borre, N. W. Henry, J. P. Zeigler, Quick selection guide to chemical protective clothing, John Wiley & Sons, Inc., Hoboken, NJ, USA 2020; T. Subbiah, G. S. Bhat, R. W. Tock, S. Parameswaran, S. S. Ramkumar, J. Appl. Polym. Sci. 2005, 96, 557.

[2] T. E. Group, The Lancet 1997, 349, 1341.

[3] P. Bajaj, A. Sengupta, Text. Prog. 1992, 22, 1; I. Holmer, Ind. Health 2006, 44, 404; M. Raheel, Protective clothing systems and materials, Vol. 25, CRC Press, 1994; S. Bhattacharjee, R. Joshi, A. A. Chughtai, C. R. Macintyre, Adv. Mater. Interfaces 2019, 6, 1900622; M. R. Bhuiyan, L. Wang, A. Shaid, R. A. Shanks, J. Ding, J. Ind. Text. 2019, 49, 97.

[4] N. Karim, S. Afroj, K. Lloyd, L. C. Oaten, D. V. Andreeva, C. Carr, A. D. Farmery, I.-D. Kim, K. S. Novoselov, ACS Nano 2020, 14, 12313.

[5] M. Parikka, Biomass and bioenergy 2004, 27, 613; S. Shafiee, E. Topal, Energy policy 2009, 37, 181; S. Shafiee, E. Topal, Energy policy 2008, 36, 775.

[6] V. K. Midha, A. Dakuri, V. Midha, J. Ind. Text. 2013, 43, 174; R. S. Rengasamy, V. K. Kothari, V. S. Bele, R. Khanna, J. Text. Inst. 2011, 102, 1019.

[7] G. Bhat, V. Narayanan, L. Wadsworth, M. Dever, Polym. Plast. Technol. Eng. 1999, 38, 499; X. Liu, S. Wahab, M. Hussain, Y. Sun, D. Kirikkaleli, J. Environ. Manage. 2021, 294, 113043; P. Selman, Landscape Research 2010, 35, 157; S. Becker, T. Bouzdine-Chameeva, A. Jaegler, J. Cleaner Prod. 2020, 274, 122739.

[8] X. Wang, F. Sun, G. Yin, Y. Wang, B. Liu, M. Dong, Sensors 2018, 18, 330; B. Sun, Y.-Z. Long, Z.-J. Chen, S.-L. Liu, H.-D. Zhang, J.-C. Zhang, W.-P. Han, J. Mater. Chem. C

2014, 2, 1209; Y. Dai, W. Liu, E. Formo, Y. Sun, Y. Xia, Polym. Advan. Tecnnol. 2011, 22, 326; T. J. Sill, H. A. Von Recum, Biomaterials 2008, 29, 1989.

[9] A. Chinnappan, C. Baskar, S. Baskar, G. Ratheesh, S. Ramakrishna, J. Mater. Chem. C 2017, 5, 12657.

[10]M. Bognitzki, T. Frese, M. Steinhart, A. Greiner, J. H. Wendorff, A. Schaper, M. Hellwig, Polym. Eng. Sci. 2001, 41, 982.

[11]G. Lomax, Coated Fabr. 1985, 15, 40; G. Lomax, Coated Fabr. 1985, 15, 115.

[12]G. R. Lomax, J. Mater. Chem. 2007, 17, 2775; J. T. Williams, Waterproof and water repellent textiles and clothing, Woodhead Publishing, 2017; S. Kara, S. Yeşilpinar, A. Akşit, Fibres Text. 2018, 2, 40.

[13]J. Ding, H. Fu, Y. Liu, J. Gao, Z. Li, X. Zhao, J. Zheng, W. Sun, H. Ni, X. Ma, Eur. Radiol. 2020, 30, 3603.

[14] https://www.grandviewresearch.com/industry-analysis/winter-wear-market (accessed: November 2021)

[15]J. C. Tanner, Coated Fabr. 1979, 8, 312; D. J. Gohlke, Coated Fabr. 1989, 18, 180; C. S. Maas, D. R. Gnepp, J. Bumpous, Arch. Otolaryngol. Head Neck Surg. 1993, 119, 1008.

[16]A. R. Tehrani-Bagha, Adv. Colloid Interface Sci. 2019, 268, 114; Q. Liu, J. Huang, J. Zhang, Y. Hong, Y. Wan, Q. Wang, M. Gong, Z. Wu, C. F. Guo, ACS Appl. Mater. Interfaces 2018, 10, 2026; J. Zhang, Q. Wu, X. Yu, P. Zha, H. Li, Mater. Lett. 2001, 48, 362; C. Fragassa, Tribology in Industry 2016, 38.

[17]K. Hu, J. Fan, X. Li, X. Gou, X. Li, X. Zhou, Medicine 2020, 99; H. Jin, C. Hong, S. Chen, Y. Zhou, Y. Wang, L. Mao, Y. Li, Q. He, M. Li, Y. Su, Stroke Vasc. Neurol. 2020, 5; Y. Xiao, M. E. Torok, Lancet Infect. Dis. 2020, 20, 523.

[18] X. Wang, B. Ding, G. Sun, M. Wang, J. Yu, Prog. Mater. Sci. 2013, 58, 1173; Y. Ding, H. Hou, Y. Zhao, Z. Zhu, H. Fong, Prog. Polym. Sci. 2016, 61, 67; R. Hu, Y. Liu, S. Shin, S. Huang, X. Ren, W. Shu, J. Cheng, G. Tao, W. Xu, R. Chen, Adv. Energy Mater. 2020, 10, 1903921.

[19] G. C. Rutledge, S. V. Fridrikh, Adv. Drug Delivery Rev. 2007, 59, 1384.

[20] S. Mohammadzadehmoghadam, Y. Dong, S. Barbhuiya, L. Guo, D. Liu, R. Umer, X. Qi, Y. Tang, in Nano-size Polymers, Springer, 2016, 89.

[21] X. Yang, J. Wang, H. Guo, L. Liu, W. Xu, G. Duan, e-Polymers 2020, 20, 682.

[22] G. M. Bose, Recherches sur la cause et sur la veritable téorie de l'électricité, Slomac, 1745.

[23] L. Rayleigh, The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science 1882, 14, 184.

[24] Cooley J F. Apparatus for electrically dispersing fluids. US, 692,631 [P]. 1902, 692: 1-6.

[25] J. Zeleny, Physical review 1917, 10, 1.

[26] Masaru H. Process for manufacturing artificial silk. Compiler: US, 1603080 [P]. 1926-10-12.

[27] Anton F. Process and apparatus for preparing artificial threads: US. 1975,504 [P]. 1934-10-2.

[28] G. I. Taylor, R. Soc. London, Sect. A: Math. Phys. Sci. 1964, 280, 383.

[29] P. K. Baumgarten, J. Colloid Interface Sci. 1971, 36, 71.

[30] D. H. Reneker, I. Chun, Nanotechnology 1996, 7, 216.

[31] S. Ramakrishna, An introduction to electrospinning and nanofibers, World scientific, 2005; W. E. Teo, S. Ramakrishna, Nanotechnology 2006, 17, R89; D. Lukáš, A. Sarkar, L. Martinová, K. Vodsed'álková, D. Lubasová, J. Chaloupek, P. Pokorný, P. Mikeš, J. Chvojka, M. Komárek, Text. Prog. 2009, 41, 59.

[32] Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, S. Ramakrishna, Compos. Sci. Technol. 2003, 63, 2223.

[33] B. Ding, M. Wang, X. Wang, J. Yu, G. Sun, Mater. Today 2010, 13, 16.

[34] X. Wang, B. Ding, J. Yu, J. Yang, Colloids Surf. B 2011, 86, 345.

[35] D. Li, Y. Xia, Adv. Mater. 2004, 16, 1151.

[36] T. Han, D. H. Reneker, A. L. Yarin, Polymer 2007, 48, 6064.

[37] R. Hartman, D. Brunner, D. Camelot, J. Marijnissen, B. Scarlett, J. Aerosol Sci. 2000, 31, 65.

[38] A. L. Yarin, S. Koombhongse, D. H. Reneker, J. Appl. Phys. 2001, 90, 4836.

[39] D. Salem, in Nanofibers and nanotechnology in textiles, Elsevier, 2007, 3.

[40] K. Garg, G. L. Bowlin, Biomicrofluidics 2011, 5, 013403.

[41] J. W. Schweizer, D. Hanson, J. Colloid Interface Sci. 1971, 35, 417.

[42] G. I. Taylor, Proc. R. Soc. London A: Math. Phys. Sci. 1969, 313, 453.

[43] S. Reznik, A. Yarin, A. Theron, E. Zussman, J. Fluid Mech. 2004, 516, 349.

[44] A. V. Subbotin, A. N. Semenov, Proc. Math. Phys. Eng. Sci. 2015, 471, 20150290.

[45] M. M. Hohman, M. Shin, G. Rutledge, M. P. Brenner, Phys. Fluids 2001, 13, 2201; M. M. Hohman, M. Shin, G. Rutledge, M. P. Brenner, Phys. Fluids 2001, 13, 2221; S. Rafiei, S. Maghsoodloo, M. Saberi, S. Lotfi, V. Motaghitalab, B. Noroozi, A. Haghi, Cellul. Chem.

Technol. 2014, 48, 401; M. Lauricella, S. Succi, E. Zussman, D. Pisignano, A. L. Yarin, Rev. of Mod. Phys. 2020, 92, 035004; S. Rafiei, S. Maghsoodloo, B. Noroozi, V. Mottaghitalab, A. Haghi, Cellul. Chem. Technol. 2013, 47, 323; M. Yousefzadeh, in Electrospun nanofibers, Elsevier, 2017, 277.

[46] S. L. Shenoy, W. D. Bates, H. L. Frisch, G. E. Wnek, Polymer 2005, 46, 3372.

[47] J. Ramos, Int. J. Numer Methods Fluids 1996, 23, 221; D. Saville, Ann. Rev. Fluid Mech. 1997, 29, 27; D. H. Reneker, A. L. Yarin, H. Fong, S. Koombhongse, J. Appl. Phys. 2000, 87, 4531; J. Feng, Phys. Fluids 2002, 14, 3912; J.-H. He, Y. Wu, N. Pang, Int. J. Nonlinear Sci. 2005, 6, 243; Y. Wan, J. Wei, J. Qiang, L. Yang, J. Fu, R. Yang, H. Wang, W. Gao, F. Ko, Adv. Sci. Lett. 2012, 10, 590; J.-W. Ha, S.-M. Yang, J. Fl. Mech. 2000, 405, 131; S. Maghsoodlou, B. Noroozi, A. K. Haghi; A. Lee, H. Jin, H.-W. Dang, K.-H. Choi, K. H. Ahn, Langmuir 2013, 29, 13630; F. Zheng, S. Zhang, J. Mo, H. Yi, S. Zhang, H. Yu, K. Lin, J. Sha, Y. Chen, Small 2020, 16, 2000397.

[48] J. M. Deitzel, J. Kleinmeyer, D. Harris, N. B. Tan, Polymer 2001, 42, 261; S. Ramakrishna, K. Fujihara, W.-E. Teo, T. Yong, Z. Ma, R. Ramaseshan, Mater. Today 2006, 9, 40; M. Beglou, A. Haghi, Cellul. Chem. Technol. 2008, 42, 441; S. Poreskandar, S. Maghsoodlou, A. Haghi, in Handbook of Research for Fluid and Solid Mechanics, Apple Academic Press, 2017, 33.

[49] S. Jian, J. Zhu, S. Jiang, S. Chen, H. Fang, Y. Song, G. Duan, Y. Zhang, H. Hou, RSC Adv. 2018, 8, 4794.

[50] I. S. Chronakis, J. Mater. Process. Tech. 2005, 167, 283.

[51] S. Kidoaki, I. K. Kwon, T. Matsuda, J. Biomed. Mater. Res., Part B 2006, 76, 219.

[52] O. Hardick, B. Stevens, D. G. Bracewell, J. Mater. Sci. 2011, 46, 3890.

[53] K. H. K. Chan, M. Kotaki, J. Appl. Polym. Sci. 2009, 111, 408.

[54] J.-H. He, Y. Liu, L.-F. Mo, Y.-Q. Wan, L. Xu, Electrospun nanofibres and their applications, ISmithers Shawbury, UK, 2008.

[55] A. Haghi, Electrospinning of nanofibers in textiles, Apple Academic Press, 2019; G. Jiang, S. Zhang, X. Qin, J. Ind. Text. 2016, 45, 483.

[56] S. Seyedin, S. Maghsoodloo, V. Mottaghitalab, Inter. J. Cheminformatics Chem. Eng. 2017, 6, 20.

[57] W. Cui, X. Li, S. Zhou, J. Weng, J. Appl. Polym. Sci. 2007, 103, 3105.

[58] M. Salehi, F. Hakkak, S. Tilebon, M. Ataeefard, M. Rafizadeh, Express Polym. Lett. 2020, 14.

[59] T. Wang, S. Kumar, J. Appl. Polym. Sci. 2006, 102, 1023.

[60] S. A. Karim, A. Sulong, C. H. Azhari, T. Lee, N. Hwei, J. Appl. Sci. Res 2012, 8, 2510; M. A. Seman, M. Khayet, N. Hilal, J. Membrane Sci. 2010, 348, 109; M. Khayet, M. A. Seman, N. Hilal, J. Membrane Sci. 2010, 349, 113.

[61] M. Essalhi, M. Khayet, C. Cojocaru, M. García-Payo, P. Arribas, The Open Nanoscience Journal 2013, 7.

[62] A. Idris, F. Kormin, M. Noordin, Sep. Purif. Technol. 2006, 49, 271.

[63] B. Rezaei, A. M. Shoushtari, M. Rabiee, L. Uzun, A. P. Turner, W. Cheung Mak, Adv. Polym. Tech. 2018, 37, 2743; N. Naderi, F. Agend, R. Faridi-Majidi, N. Sharifi-Sanjani, M. Madani, J. Nanosci. Nanotechno. 2008, 8, 2509; M. Ziabari, V. Mottaghitalab, A. K. Haghi, Korean J. Chem. Eng. 2010, 27, 340; M. Kanafchian, M. Valizadeh, A. K. Haghi, Korean J. of Chem. Eng. 2011, 28, 428; M. K. Sadan, H.-J. Ahn, G. Chauhan, N. Reddy, Euro. Polym. J. 2016, 74, 91.

[64] M. Mohammadian, A. Haghi, Mater. Plast. 2012, 49, 301; S. Y. Gu, J. Ren, Macromol. Mater. Eng. 2005, 290, 1097; H. Maleki, A. A. Gharehaghaji, G. Criscenti, L. Moroni, P. J.

Dijkstra, J. Appl. Polym. Sci. 2015, 132; L. Kong, G. R. Ziegler, Carbohydr. Polym. 2013, 92, 1416.

[65] B. H. Moghadam, A. K. Haghi, S. Kasaei, M. Hasanzadeh, J. Macromol. Sci. B 2015, 54, 1404; B. H. Moghadam, M. Hasanzadeh, A. Haghi, System 2013, 22, 23.

[66] P. Vass, E. Szabó, A. Domokos, E. Hirsch, D. Galata, B. Farkas, B. Démuth, S. K. Andersen, T. Vigh, G. Verreck, Wiley Interdiscip. Rev. Nanomed. Nanobiotechnol. 2020, 12, e1611.

[67] S. Omer, L. Forgách, R. Zelkó, I. Sebe, Pharmaceutics 2021, 13, 286.

[68] S. Theron, A. Yarin, E. Zussman, E. Kroll, Polymer 2005, 46, 2889; Y. Yang, Z. Jia, Q. Li, L. Hou, H. Gao, L. Wang, Z. Guan, "Multiple jets in electrospinning", presented at 2006 IEEE 8th International Conference on Properties & applications of Dielectric Materials, 2006; G. Nie, Z. Zhang, T. Wang, C. Wang, Z. Kou, ACS Appl. Mater. Interfaces 2021, 13, 37961.

[69] Jirsak O, Sanetrnik F, Lukas D, et al. Method of nanofibres production from a polymer solution using electrostatic spinning and a device for carrying out the method: US 7,585,437 [P]. 2009-9-8.

[70] H. Niu, T. Lin, Journal of nanomaterials 2012, 2012; J. Holopainen, T. Penttinen, E. Santala, M. Ritala, Nanotechnology 2014, 26, 025301.

[71] M. Kurecic, M. S. Smole, Tekstilec 2013, 56; M. B. Bazbouz, H. Liang, G. Tronci, Mater. Sci. Eng. C 2018, 91, 541.

[72] C. Mingjun, Z. Youchen, L. Haoyi, L. Xiangnan, D. Yumei, M. M. Bubakir, Y. Weimin, Adv. Ind. Eng. Polym. Res. 2019, 2, 110.

[73] F. Muller, S. Zainuddin, T. Scheibel, Molecules 2020, 25, 5540.

[74] T. D. Brown, P. D. Dalton, D. W. Hutmacher, Prog. Polym. Sci. 2016, 56, 116.

[75] H. Li, H. Chen, X. Zhong, W. Wu, Y. Ding, W. Yang, J. Appl. Polym. Sci. 2014, 131.

[76] P. Martins, A. Lopes, S. Lanceros-Mendez, Prog. Polym. Sci. 2014, 39, 683; F. Liu, N. A. Hashim, Y. Liu, M. M. Abed, K. Li, J. Membrane Sci. 2011, 375, 1; G.-d. Kang, Y.-m. Cao, J. Membrane Sci. 2014, 463, 145.

[77] A. J. Lovinger, in Developments in crystalline polymers—1, Springer, 1982, 195.

[78] G. Jiang, L. Luo, L. Tan, J. Wang, S. Zhang, F. Zhang, J. Jin, ACS Appl. Mater. Interfaces 2018, 10, 28210.

[79] K. S. Han, S. Lee, M. Kim, P. Park, M. H. Lee, J. Nah, Adv. Funct. Mater. 2019, 29, 1903633.

[80] L. Lan, J. Xiong, D. Gao, Y. Li, J. Chen, J. Lv, J. Ping, Y. Ying, P. S. Lee, ACS Nano 2021, 15, 5307.

[81] C. Seoul, Y. T. Kim, C. K. Baek, J. Polym. Sci., Part B: Polym. Phys. 2003, 41, 1572.

[82] M. Zhang, J. Sheng, X. Yin, J. Yu, B. Ding, Macromol. Mater. Eng. 2017, 302.

[83] F. Hakkak, M. Rafizadeh, J. Macromol. Sci. B 2013, 52, 1250.

[84] J. Li, S. Xu, M. Hassan, J. Shao, L. F. Ren, Y. He, J. Appl. Polym. Sci. 2019, 136, 47125.

[85] Z. Li, J. Shen, I. Abdalla, J. Yu, B. Ding, Nano Energy 2017, 36, 341.

[86] Q. Qiu, M. Zhu, Z. Li, K. Qiu, X. Liu, J. Yu, B. Ding, Nano Energy 2019, 58, 750.

[87] B. Ding, J. Yu, Electrospun nanofibers for energy and environmental applications, Springer, 2014.

[88] Sharmin E, Zafar F. Polyurethane, 2012, 3-16.

[89] D. Feldman, Designed monomers and polymers 2008, 11, 1.

[90] G. T. Howard, International Biodeterioration & Biodegradation 2002, 49, 245.

[91] W. Zhou, X. Gong, Y. Li, Y. Si, S. Zhang, J. Yu, B. Ding, Chem. Eng. J. 2022, 427, 130925.

[92] J. Zhao, Y. Li, J. Sheng, X. Wang, L. Liu, J. Yu, B. Ding, ACS Appl. Mater. Interfaces 2017, 9, 29302.

[93] Y. K. Kang, C. H. Park, J. Kim, T. J. Kang, Fibers Polym. 2007, 8, 564.

[94] Y. Li, Z. Zhu, J. Yu, B. Ding, ACS Appl. Mater. Interfaces 2015, 7, 13538.

[95] D. Miao, Z. Huang, X. Wang, J. Yu, B. Ding, Small 2018, 14, 1801527.

[96] L. Marmoret, M. Lewandowski, A. Perwuelz, Transp Porous Media 2012, 93, 79.

[97] T.-C. Codau, E. Onofrei, S. Petrusic, G. Bedek, D. Dupont, D. Soulat, J. Porous Media 2015, 18.

[98] A. Rabbi, K. Nasouri, H. Bahrambeygi, A. M. Shoushtari, M. R. Babaei, Fibers Polym. 2012, 13, 1007.

[99] M. Gorji, A. Sadeghian Maryan, J. Ind. Text. 2018, 47, 1645.

[100] W. Zhou, X. Gong, Y. Li, Y. Si, S. Zhang, J. Yu, B. Ding, J. Colloid Interface Sci. 2021, 602, 105.

[101] H. Wu, L. Zhao, S. Zhang, Y. Si, J. Yu, B. Ding, ACS Appl. Mater. Interfaces 2021, 13, 18165.

[102] P.-C. Hsu, A. Y. Song, P. B. Catrysse, C. Liu, Y. Peng, J. Xie, S. Fan, Y. Cui, Science 2016, 353, 1019.

[103] P.-C. Hsu, X. Liu, C. Liu, X. Xie, H. R. Lee, A. J. Welch, T. Zhao, Y. Cui, Nano lett. 2015, 15, 365; P.-C. Hsu, C. Liu, A. Y. Song, Z. Zhang, Y. Peng, J. Xie, K. Liu, C.-L. Wu, P. B. Catrysse, L. Cai, Sci. Adv. 2017, 3, e1700895.

[104] X. A. Zhang, S. Yu, B. Xu, M. Li, Z. Peng, Y. Wang, S. Deng, X. Wu, Z. Wu, M. Ouyang, Science 2019, 363, 619; J. Hu, M. Irfan Iqbal, F. Sun, Adv. Funct. Mater. 2020, 30, 2005033.

[105] H. Zhuo, J. Hu, S. Chen, L. Yeung, J. Appl. Polym. Sci. 2008, 109, 406; L. Tan, J. Hu, H. Zhao, Mate. Lett. 2015, 156, 46; L. Tan, J. Hu, H. Huang, J. Han, H. Hu, Inter. J. Bio. Macromol. 2015, 79, 469.

[106] P. Slade, Thermochim Acta 1970, 1, 459; P. Dunn, B. Ennis, Thermochim Acta 1971, 3, 81.

[107] W. Yan, D. Miao, A. A. Babar, J. Zhao, Y. Jia, B. Ding, X. Wang, J. Colloid Interface Sci. 2020, 565, 426.

[108] C. Drew, X. Wang, K. Senecal, H. Schreuder-Gibson, J. He, J. Kumar, L. A. Samuelson, J. Macromol. Sci. A 2002, 39, 1085.

[109] J. Wang, Y. Li, H. Tian, J. Sheng, J. Yu, B. Ding, RSC Adv. 2014, 4, 61068.

[110] J. Sheng, M. Zhang, W. Luo, J. Yu, B. Ding, RSC Adv. 2016, 6, 29629.

[111] A. A. Babar, X. Wang, N. Iqbal, J. Yu, B. Ding, Adv. Mater. Interfaces 2017, 4, 1700062.

[112] D. Miao, X. Wang, J. Yu, B. Ding, Adv. Funct. Mater. 2021, 31, 2008705.

[113] S. Gu, J. Ren, G. Vancso, Euro. Polym. J. 2005, 41, 2559; R. A. Abuzade, A. Zadhoush, A. A. Gharehaghaji, J. Appl. Polym. Sci. 2012, 126, 232.

[114] Y. Jiang, K. Dong, J. An, F. Liang, J. Yi, X. Peng, C. Ning, C. Ye, Z. L. Wang, ACS Appl. Mater. Interfaces 2021, 13, 11205.

[115] S. Guo, B. Yu, A. Ahmed, H. Cong, Y. Shen, J. of Hazard. Mater. 2021, 127602; J. Xiong, W. Shao, L. Wang, C. Cui, Y. Jin, H. Yu, P. Han, Y. Gao, F. Liu, Q. Ni, Macromol. Mater. Eng. 2021, 306, 2100371.

[116] K. Liu, L. Deng, T. Zhang, K. Shen, X. Wang, Ind. Eng. Chem. Res. 2020, 59, 4447.

[117] S. Ribeiro, P. Costa, C. Ribeiro, V. Sencadas, G. Botelho, S. Lanceros-Méndez, Composites, Part B 2014, 67, 30.

[118] M. W. Frey, Polym. Rev. 2008, 48, 378.

[119] S. Shi, K. Zhu, X. Chen, J. Hu, L. Zhang, ACS Sustain. Chem. Eng. 2019, 7, 19799.

[120] T. Zhang, Z. Xu, J. Zhao, L. Huang, Macromol. Mater. Eng. 2020, 305, 2000370.

[121] R. Sen, B. Zhao, D. Perea, M. E. Itkis, H. Hu, J. Love, E. Bekyarova, R. C. Haddon, Nano Lett. 2004, 4, 459.

[122] Z. Ma, Q. Huang, Q. Xu, Q. Zhuang, X. Zhao, Y. Yang, H. Qiu, Z. Yang, C. Wang, Y. Chai, Nat. Mater. 2021, 20, 859.

[123] Y. Wang, L. Chen, H. Cheng, B. Wang, X. Feng, Z. Mao, X. Sui, Chem. Eng. J. 2020, 402, 126222.

[124] A. K. An, J. Guo, E.-J. Lee, S. Jeong, Y. Zhao, Z. Wang, T. Leiknes, J. Membrane Sci. 2017, 525, 57.

[125] B. Ding, T. Ogawa, J. Kim, K. Fujimoto, S. Shiratori, Thin Solid Films 2008, 516, 2495.

[126] S. Wen, L. Liu, L. Zhang, Q. Chen, L. Zhang, H. Fong, Mate. Lett. 2010, 64, 1517.

[127] W. Zhou, X. Yu, Y. Li, W. Jiao, Y. Si, J. Yu, B. Ding, ACS Appl. Mater. Interfaces 2020, 13, 2081.

[128] P. He, F. Wu, M. Yang, W. Jiao, X. Yin, Y. Si, J. Yu, B. Ding, Compos. Commun. 2021, 25, 100720.

[129] T. Padmanabhan, V. Kamaraj, L. Magwood Jr, B. Starly, J. Manuf. Process. 2011, 13, 104; P. Filip, P. Peer, "Electrospinning of poly (ethylene oxide) solutions-Quantitative relations between mean nanofibre diameter, concentration, molecular weight, and viscosity", presented at AIP Conference Proceedings, 2019; A. Maurya, P. Narayana, A. G. Bhavani, H. Jae-Keun, J.-T. Yeom, N. Reddy, J. Electrostat. 2020, 104, 103425; S. Ö. Gönen, M. E. Taygun, S. Küçükbayrak, Chem. Eng. Tech. 2015, 38, 844; P. Agarwal, P. Mishra, P. Srivastava, J. Mater. Sci. 2012, 47, 4262; T. Khatti, H. Naderi-Manesh, S. M. Kalantar, Neural. Comput. Appl. 2019, 31, 239.

[130] K.-Y. Law, J. Phys. Chem. Lett. 2014, 5, 686−688

[131] H. A. Güleç, K. Sarıogˇlu, M. Mutlu, J. Food Eng. 2006, 75, 187.

[132] J.-L. Liu, X.-Q. Feng, G. Wang, S.-W. Yu, J. Phys.: Condens. Matter 2007, 19, 356002.

[133] A. Nakajima, K. Hashimoto, T. Watanabe, Molecular Materials and Functional Polymers 2001, 31.

[134] N. Hilal, M. Khayet, C. J. Wright, Membrane modification: Technology and applications, CRC press, 2012.

[135] Y. Li, F. Yang, J. Yu, B. Ding, Adv. Mater. Interfaces 2016, 3, 1600516.

[136] J. Sheng, M. Zhang, Y. Xu, J. Yu, B. Ding, ACS Appl. Mater. Interfaces 2016, 8, 27218.

[137] Y. Yu, F. Zhang, Y. Liu, Y. Zheng, B. Xin, Z. Jiang, X. Peng, S. Jin, J. Mater. Res. 2020, 35, 1173.

[138] X. Gu, N. Li, J. Cao, J. Xiong, Polym. Eng. Sci. 2018, 58, 1381.

[139] C. Zeng, H. Wang, H. Zhou, T. Lin, Adv. Mater. Interfaces 2016, 3, 1600036.

[140] A. A. Babar, X. Zhao, X. Wang, J. Yu, B. Ding, J. Colloid Interface Sci. 2020, 577, 207.

[141] J. Ju, Z. Shi, N. Deng, Y. Liang, W. Kang, B. Cheng, RSC Adv. 2017, 7, 32155.

[142] L. Jiang, Y. Zhao, J. Zhai, Angew. Chem. 2004, 116, 4438.

[143] D. Li, Y. Xia, Nano Lett. 2004, 4, 933.

[144] B. Dai, K. Li, L. Shi, X. Wan, X. Liu, F. Zhang, L. Jiang, S. Wang, Adv. Mater. 2019, 31, 1904113.

[145] X. Wang, Z. Huang, D. Miao, J. Zhao, J. Yu, B. Ding, ACS Nano 2018, 13, 1060.

[146] K. Acatay, E. Simsek, C. Ow- Yang, Y. Z. Menceloglu, Angew. Chem. 2004, 116, 5322.

[147] Y. Zhao, X. Cao, L. Jiang, J. Am. Chem. Soc. 2007, 129, 764.

[148] S. K. Tiwari, S. S. Venkatraman, Mater. Sci. and Eng. C 2012, 32, 1037.

[149] X. Wang, Q. Wang, F. Huang, Q. Wei, Fibers Polym. 2016, 17, 624.

[150] S. Rafiei, B. Noroozi, L. Heltai, A. K. Haghi, J. Ind. Text. 2018, 47, 1791; J. Yoon, H. S. Yang, B. S. Lee, W. R. Yu, Adv. Mater. 2018, 30, 1704765.

[151] Y. Miyauchi, B. Ding, S. Shiratori, Nanotechnology 2006, 17, 5151.

[152] Y. Liu, J.-H. He, Int. J. Nonlinear Sci. 2007, 8, 393.

[153] X. Yu, Y. Li, X. Wang, Y. Si, J. Yu, B. Ding, ACS Appl. Mater. Interfaces 2020, 12, 32078.

[154] Q. Zhuang, Z. Ma, Y. Gao, Y. Zhang, S. Wang, X. Lu, H. Hu, C. Cheung, Q. Huang, Z. Zheng, Adv. Funct. Mater. 2021, 31, 2105587.

[155] S. Feng, Z. Zhong, Y. Wang, W. Xing, E. Drioli, J. Membrane Sci. 2018, 549, 332.

[156] X. Li, J. Lin, F. Bian, Y. Zeng, J. Polym. Sci., Part B: Polym. Phys. 2018, 56, 36.

[157] S. Liu, L. Li, R. Liu, J. Liu, X. Zhao, X. Liao, J. Phys. D 2020, 53, 195403.

[158] L. Yi, S. Wang, L. Wang, J. Yao, J. Marek, M. Zhang, J. Appl. Polym. Sci. 2021, 138, 50391.

[159] G. Amini, M. Karimi, F. Zokaee Ashtiani, J. Ind. Text. 2020, 1528083720904675.

[160] P. Li, Q. Zhang, T. T. Chadyagondo, G. Li, H. Gu, N. Li, Fibers Polym. 2020, 21, 1444.

[161] B. Yoon, S. Lee, Fibers Polym. 2011, 12, 57.

[162] Y. Xu, J. Sheng, X. Yin, J. Yu, B. Ding, J. Colloid Interface Sci. 2017, 508, 508.

[163] Y. Yu, Y. Liu, F. Zhang, S. Jin, Y. Xiao, B. Xin, Y. Zheng, Fibers Polym. 2020, 21, 954.

[164] M. N. Liu, X. Yan, M. H. You, J. Fu, G. D. Nie, M. Yu, X. Ning, Y. Wan, Y. Z. Long, J. Appl. Polym. Sci. 2018, 135, 46342.

[165] J. Gu, H. Gu, J. Cao, S. Chen, N. Li, J. Xiong, Appl. Surf. Sci. 2018, 439, 589.

[166] W. Zhou, X. Yu, L. Cao, M. Yang, Y. Li, Y. Si, J. Yu, B. Ding, Adv. Sustain. Syst. 2020, 4, 2000105.

[167] J. Zhao, X. Wang, L. Liu, J. Yu, B. Ding, ACS Appl. Mater. Interfaces 2018, 10, 30887.

[168] G. Amini, S. Samiee, A. A. Gharehaghaji, F. Hajiani, Adv. Polym. Tech. 2016, 35, 419.

[169] W. Zhu, J. Zhao, X. Wang, X. Liu, J. Yu, B. Ding, J. Colloid Interface Sci. 2019, 556, 541.

[170] H. Cui, Y. Li, X. Zhao, X. Yin, J. Yu, B. Ding, Compos. Commun. 2017, 6, 63.

[171] X. Gu, N. Li, H. Gu, X. Xia, J. Xiong, J. Appl. Polym. Sci. 2018, 135, 46360.

[172] J. Zhao, W. Zhu, W. Yan, X. Wang, L. Liu, J. Yu, B. Ding, Compos. Commun. 2019, 15, 40.

[173] J. Sheng, Y. Xu, J. Yu, B. Ding, ACS Appl. Mater. Interfaces 2017, 9, 15139.

[174] J. Sheng, Y. Li, X. Wang, Y. Si, J. Yu, B. Ding, Sep. Purif. Technol. 2016, 158, 53.

[175] Y. Guo, W. Zhou, L. Wang, Y. Dong, J. Yu, X. Li, B. Ding, ACS Applied Bio Materials 2019, 2, 5949.

[176] Y. S. Park, J. W. Lee, Y. S. Nam, W. H. Park, J. Appl. Polym. Sci. 2015, 132.

[177] M. Gorji, M. Karimi, S. Nasheroahkam, J. Ind. Text. 2018, 47, 1166.

[178] J. Zhao, X. Wang, Y. Xu, P. He, Y. Si, L. Liu, J. Yu, B. Ding, ACS Appl. Mater. Interfaces 2020, 12, 15911.

[179] Y. Yue, X. Gong, W. Jiao, Y. Li, X. Yin, Y. Si, J. Yu, B. Ding, J. Colloid Interface Sci. 2021, 592, 310.

[180] Y. Wang, G. Xia, H. Yu, B. Qian, Y. H. Cheung, L. H. Wong, J. H. Xin, Adv. Mater. 2021, 33, 2100140.

[181] H. Venkatesan, J. Chen, H. Liu, W. Liu, J. Hu, Adv. Funct. Mater. 2020, 30, 2002437.

[182] V. Novák, Evapotranspiration in the soil-plant-atmosphere system, Springer Science & Business Media, 2012; G. Chavarria, H. P. dos Santos, Embrapa Uva e Vinho-Capítulo em livro científico (ALICE) 2012.

[183] A. A. Babar, D. Miao, N. Ali, J. Zhao, X. Wang, J. Yu, B. Ding, ACS Appl. Mater. Interfaces 2018, 10, 22866.

[184] T. Yun, H. Kim, A. Iqbal, Y. S. Cho, G. S. Lee, M. K. Kim, S. J. Kim, D. Kim, Y. Gogotsi, S. O. Kim, Adv. Mater. 2020, 32, 2070064.

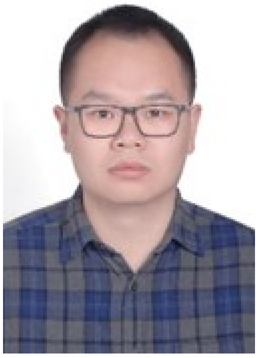
[185] Z. Zeng, F. Jiang, Y. Yue, D. Han, L. Lin, S. Zhao, Y. B. Zhao, Z. Pan, C. Li, G. Nyström, Adv. Mater. 2020, 32, 1908496.

[186] M. A. Heald, J. B. Marion, Classical electromagnetic radiation, Courier Corporation, 2012.

[187] S. Biswas, S. S. Panja, S. Bose, J. Mater. Chem. C 2018, 6, 3120.

[188] L. Cai, H. Shao, X. Hu, Y. Zhang, ACS Sustain. Chem. Eng. 2015, 3, 2551.

Biography



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Electrospinning has been used for several applications over the last 20 years. We review multifunctional protective membranes in terms of novel material design, novel structure construction, and various applications via electrospinning. Diverse protective membranes are investigated, existing problems are discussed, and solutions for future technology development are proposed. This is of significance for the sustainable development of intelligent protection systems.

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Recent progress in protective membranes fabricated via electrospinning: Adv. Mater., biomimetic structures, and functional applications