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Research progress in preparation, properties, and applications of medical protective fiber materials

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ABSTRACT

A variety of public health events seriously threaten human life and health, especially the outbreak of COVID-19 at the end of 2019 has caused a serious impact on human production and life. Wearing personal protective equipment (PPE) is one of the most effective ways to prevent infection and stop the spread of the virus. Medical protective fiber materials have become the first choice for PPE because of their excellent barrier properties and breathability. In this article, we systematically review the latest progress in preparation technologies, properties, and applications of medical protective fiber materials. We first summarize the technological characteristics of different fiber preparation methods and compare their advantages and disadvantages. Then the barrier properties, comfort, and mechanical properties of the medical protective fiber materials used in PPE are discussed. After that, the applications of medical protective fibers in PPE are introduced, and protective clothing and masks are discussed in detail. Finally, the current status, future development trend, and existing challenges of medical protective fiber materials are summarized.

1. Introduction

As of Sep. 18th, 2022, the latest data released by the World Health Organization show that the cumulative number of confirmed coronavirus disease 2019 (COVID-19) cases in more than 200 countries and regions worldwide has reached 609 million, with more than 6.5 million deaths. The major outbreak of COVID-19 has undoubtedly had a serious impact on existing medical facilities, economic systems, the environment, social and cultural life, and personal freedom [1–4]. The main transmission mode of coronavirus is through respiratory droplets, in the same way as common viruses [5]. Effective measures to reduce the impact of COVID-19 include eliminating the source of infection, interrupting the transmission pathway of the virus, and vaccination. Wearing personal protective equipment (PPE) has proven to be an effective way to stop the spread of the virus [6].

According to the Occupational Safety and Health Administration (OSHA), PPE is “equipment worn to reduce exposure to risks that cause serious work-related injuries and illnesses”. During the COVID-19 epidemic, the demand for PPE has increased dramatically around the world. Most PPE is usually made of fibrous fabrics, both natural and synthetic [7]. Natural fibers are abundant, biodegradable, and

renewable in nature. Fabrics made from natural fibers, such as cotton fibers, have good breathability, water absorption, softness, and comfort, but poor mechanical strength, durability, and barrier properties. Compared with natural fibers, synthetic fibers have lower manufacturing costs, better strength, and wear resistance, and have been widely used in biomedical, filtration, and medical protection fields [8–10].

Medical protective fabrics with excellent barrier properties can be prepared by weaving, knitting, and nonwoven techniques. Among them, nonwoven technology is the most widely used due to the simple process. Nonwoven protective materials made of petroleum-derived polymers, such as polypropylene (PP), polyethylene (PE) and polyethylene terephthalate (PET), have good hydrophobicity and barrier properties and have been widely used in disposable personal protective clothing and surgical masks [11,12]. These nonwoven PPE can effectively intercept all kinds of pathogenic microorganisms and liquids and play an important role in protecting medical staff and the general public from pathogenic microorganisms (Fig. 1).

In this article, we presented the research progress on the processing technologies, properties, and applications of medical protective fiber materials. We first introduced various spinning processes for preparing

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medical protective fiber materials and summarized the advantages and disadvantages of these spinning processes and the resultant fiber materials. Then, the properties of medical protective fiber materials, including barrier properties, comfort, and mechanical properties were discussed. After that, the application status of medical protective fiber materials was reviewed. Finally, the existing problems, challenges, and future development of medical protective fiber materials were put forward.

2. Processing technology of medical protective fiber materials

PPE is usually manufactured with medical protective fabrics obtained by weaving, knitting, or nonwoven techniques [13]. The fibers commonly used for weaving and knitting have large diameters and large pores between the fibers, so the barrier properties of the woven and knitted fabrics are poor [14]. The barrier properties of woven and knitted fabrics can be effectively improved by adjusting the fiber structure or introducing other fiber components, but the production cost will be significantly increased. The most popular fabric used in PPE is micro/nanofiber nonwoven. Unlike woven and knitted fabrics, which are geometrically structured, nonwoven fabrics are produced by hot pressing or solvent treatment of randomly distributed micro/nanofibers. In addition, nonwoven fabrics show better protection against pathogenic microorganisms and liquids due to the small diameter of nonwoven fibers.

There are many technologies for preparing micro/nanofibers, such as spun-bonded technology, melt-blown technology, electrospinning, centrifugal spinning, solution blow spinning, and flash spinning [15–20]. These spinning methods have their advantages and disadvantages and the fiber materials prepared by these methods have their application fields (Table 1). In this section, we reviewed the development process of these spinning technologies, the structures of the spinning devices, the principles of the spinning methods, and the characteristics of the resultant micro/nanofibers.

2.1. Spun-bonded technology

Spun-bonded technology involves spinning a molten polymer into a fibrous web and bonding the web to a piece of nonwoven fabric. Spun-bonded technology originated in the 1940s and was commercialized by Freudenberg and DuPont in the 1950s. Further improvements to the spun-bonded technology, including encapsulation, quenching, and drawing devices, were made by Matsuke et al. and Kimberly–Clark in 1974 and 1982, respectively [31]. Hills patented a multicomponent spun-bonded process in 1992, which can produce multicomponent fibers by changing the number and structure of extruders or using more complex spinning packages [32]. After years of development, spun-bonded technology has been industrialized due to its high productivity.

A typical spun-bonded device consists mainly of the extruder, metering pump, spinneret, quenching chamber, attenuator, collector, bonding, and winding devices (Fig. 2a) [21]. The preparation of fiber materials by the spun-bonded process includes five steps: fiber formation, quenching, stretching, bonding, and winding. Polymers are blended in an extruder, and then the molten polymers are extruded through the spinneret. The polymer jets enter the quenching chamber and are rapidly solidified into fibers under the action of cold air. During the attenuation process, the fibers are stretched, resulting in a reduction of the fiber diameter. After that, the resulting microfibers are deposited on the conveyor belt and formed into a fiber web under negative pressure. Finally, the fiber web is transported to the bonding zone where it is thermally bonded and/or chemically bonded to produce a nonwoven fabric.

The formation of the microfiber web is affected by several processing parameters, including air velocity, conveyor movement speed, bonding time, bonding surface temperature, bonding pressure, etc. The structures and properties of the spun-bonded fibers depend on the dynamics of the polymer jet and the effect of air resistance, which are closely related to the draft deformation and crystallization during fiber solidification [33]. Compared with the woven and knitted fibers, the

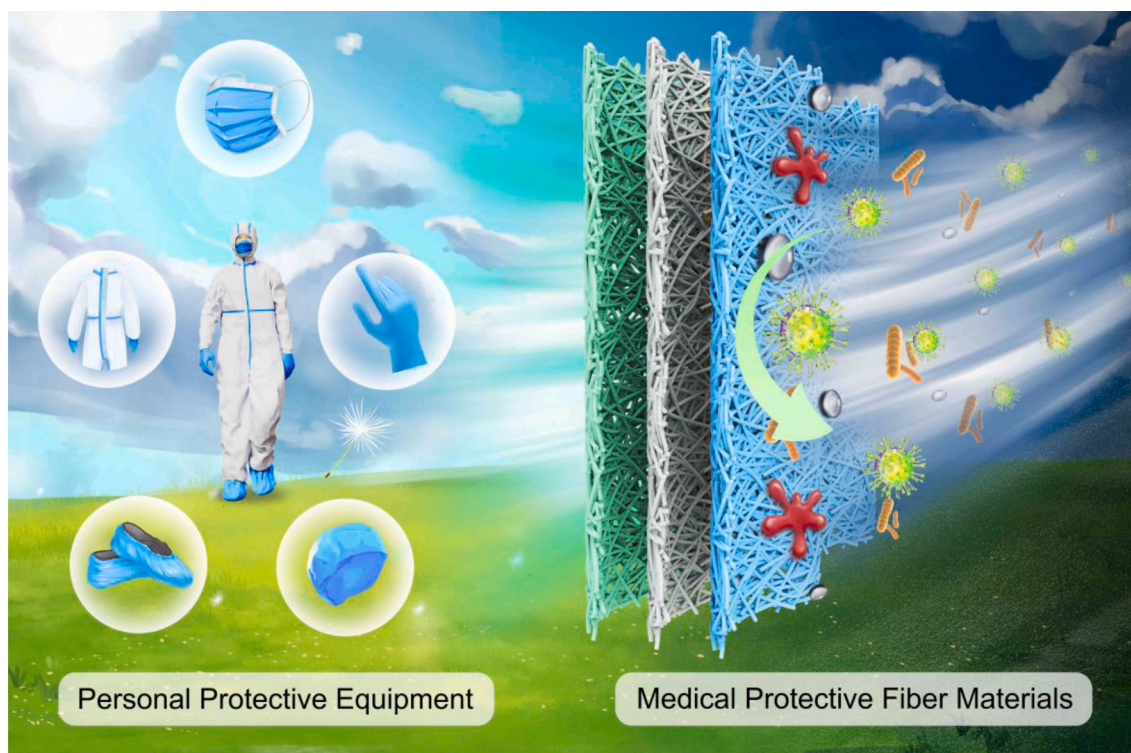
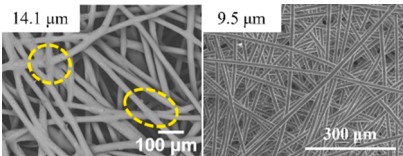
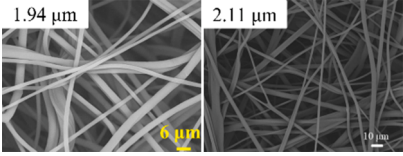
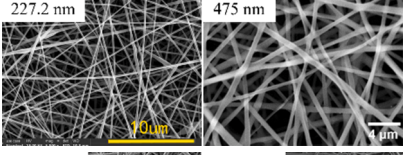
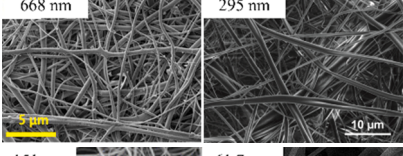
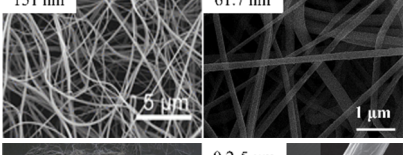
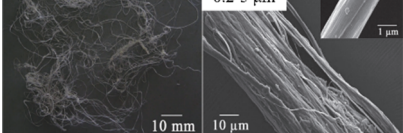


Fig. 1. Schematic showing a variety of PPE made of medical protective fiber materials and their protection mechanism against pathogenic microorganisms and liquids.

Table 1
The advantages and disadvantages of micro/nanofiber nonwoven manufactured by different spinning technologies.

Processing technique	Dimensions/microstructure		Advantages	Disadvantages
(a) Spun-bonded	Microfibers [21,22]		High mechanical strength Large-scale fabrication	Poor barrier property Larger diameter
(b) Melt-blown	Micro/nanofibers [23,24]		High barrier property Solvent-free Large-scale fabrication Wide range of materials	Poor mechanical strength Larger diameter High temperature
(c) Electrospinning	Nanofibers [25,26]		High barrier property Simple device Ultrafine diameter Wide range of materials	Poor mechanical strength High voltage Low productivity
(d) Centrifugal spinning	Nanofibers [27,28]		High barrier property Wide range of materials	Poor mechanical strength Complex device Oriented fiber structure
(e) Solution blow spinning	Nanofibers [29,30]		High barrier property No voltage Wide range of materials Ultrafine diameter	Poor mechanical strength Easy to form fiber bundles
(f) Flash spinning	Micro/nanofibers [20]		High barrier property High mechanical strength Good permeability	Easy to form fiber bundles

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microfiber nonwoven prepared by spun-bonded technology has many superior properties, such as randomly oriented fiber structure, high tear strength, good thermal properties, permeability, and abrasive resistance [15]. Therefore, spun-bonded fibers have been widely used in many fields, such as construction, medical and health care, agricultural packaging, and protective materials, etc [34–37].

A bicomponent PP@PE electret microfiber material with a diameter of 14 μm was prepared by spun-bonded technology (Fig. 2b and c). The fiber materials are charged by electrostatic electret to improve their interception efficiency of particulate matters. Despite the presence of electric charges on the spun-bonded materials, the filtration efficiency of the fiber material can only reach 88.27%, which can be attributed to the large diameter of the fibers prepared by the spun-bonded method (Fig. 2d). In order to improve the protective properties of fiber materials, reducing the fiber diameter is an effective strategy.

2.2. Melt-blown technology

Melt-blown technology is a simple and facile spinning process that allows the production of micro/nanofiber webs with random structures. This technology was developed by the U.S. Naval Research Laboratory in the 1950s to detect radiation after nuclear tests [38]. In the 1960s, Esso patented and commercialized the “melt-blown process”, becoming one

of the earliest commercial practitioners of melt-blown technology [39]. From 1970 to the present (July 6, 2022), 8036 patents on melt-blown technology and the development of nonwoven fabrics using melt-blown technology have been filed or granted, as retrieved from the Web of Science.

The melt-blown equipment consists of five main components: an extruder, a metering pump, a spinneret, a collector, and a winding device [40]. Polymers are fed to the extruder with a hopper at a certain feeding rate (Fig. 3a) [23]. Then the extruder supplies the molten polymers to a metering pump. The molten polymers are extruded through the spinneret and drawn to refine under the action of high temperature and high-speed airflow. With the extension of the distance from the spinneret, the polymer jets gradually cool and solidify, and are finally collected by a collector. The diameter of micro/nanofibers mainly depends on extrusion speed, polymer melt viscosity and temperature, airflow temperature, and speed [41].

Melt-blown technology uses high-speed and high-temperature airflow to draft the molten polymer to form a continuous network of micro/nano fibers in one step. Compared to spun-bonded technology, melt-blown technology offers significant cost advantage and high productivity. Compared with some existing solution spinning methods, such as electrospinning and solution blow spinning, melt-blown spinning does not require solvents, has no pollution problem, and is more

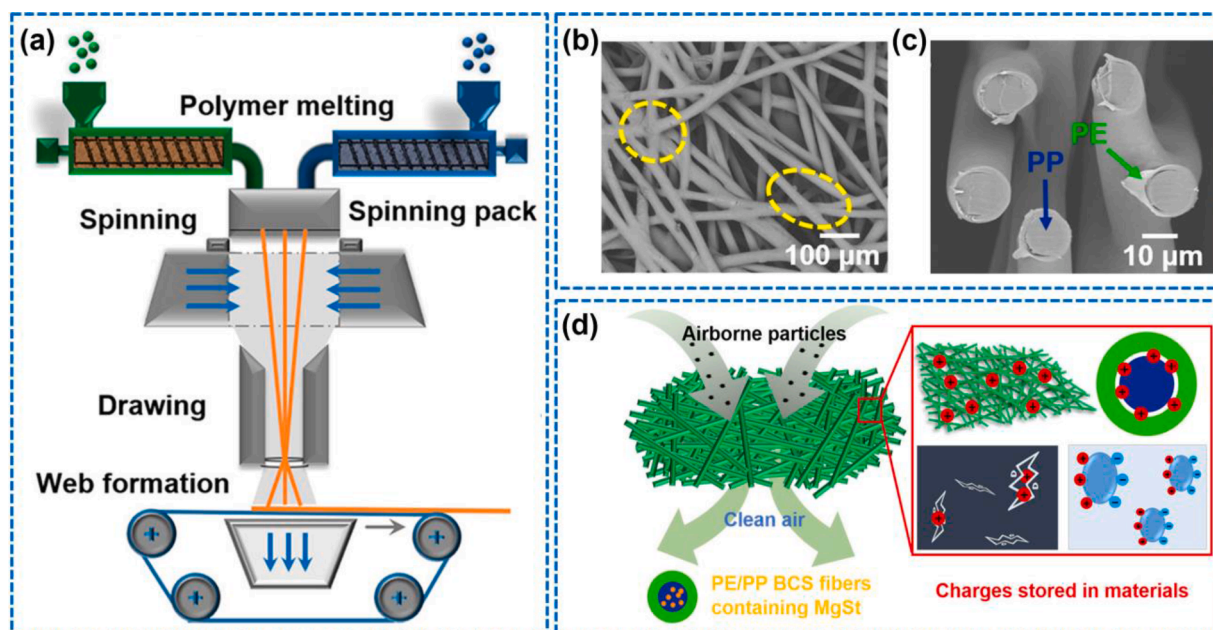


Fig. 2. Preparation of nonwovens with spun-bonded technology. (a) Schematic diagram of a typical spun-bonded device. (b) SEM image of the bicomponent polypropylene@polyethylene (PP@PE) microfibers prepared by spun-bonded technology. (c) Cross-sectional SEM image of the bicomponent PP@PE microfibers. (d) Filtration mechanism of particulate matters by the PP@PE electret material. Reproduced with permission from Ref. [21]. Copyright 2019 American Chemical Society.

efficient. With the rapid increase in social productivity and the global emphasis on environmental protection, as well as global security emergencies such as COVID-19, melt-blown technology is growing rapidly worldwide, and the product market is expanding [43]. However, similar to spun-bonded technology, few polymers are suitable for melt-blown technology to prepare micro/nanofibers [44–46].

The micro/nanofiber nonwoven made by the melt-blown method has a large specific surface area, small pore size, and high porosity, which is suitable for air filtration [47]. A bicomponent PP/P(VDF-TrFE) micro/nanofiber nonwoven material was prepared by melt-blown technology, demonstrating a filtration efficiency of higher than 90% (Fig. 3b) [42]. In addition to air filtration, melt-blown nonwoven fabrics are also widely used in liquid filtration, oil/water separation, medical protection, and other fields [48–51]. During the COVID-19 epidemic, the wearing of surgical masks with superior filtration properties made by melt-blown technology played an important role in personal protection [43]. Although the nonwoven fabrics prepared by melt-blown technology have good filtration efficiency, the filtration property cannot meet the application requirements without electrostatic electret, and the mechanical properties and wear resistance of these nonwoven fabrics are poor.

2.3. Electrospinning

Electrospinning is one of the most used nanofabrication techniques in the last three decades, and it can produce continuous nanofibers with superior properties from a wide range of polymers and polymer composites [52]. In 1887, Charles discovered electrospinning while studying e-spinning, which led to the term electrospinning. In 1902, Cooley applied for a patent for electrospinning and described the spinning process [53]. Anton patented the process and equipment for electrospinning in 1934, which led to the early commercialization of electrospinning technology [54]. In the 21st century, electrospinning has received a great deal of attention from researchers and industry, and various electrospinning technologies have been developed, including single-nozzle electrospinning, multi-nozzle electrospinning, co-axial electrospinning, needleless electrospinning, and melt electrospinning (Fig. 4) [55–59].

A conventional electrospinning device consists of four basic components: a high-voltage power supply, an injection pump, a spinneret with a capillary tube, and a vertical or horizontal collector (Fig. 4a) [60]. The spinning solution forms droplets at a specific concentration and conductivity during the electrospinning process. The droplets are subsequently stretched and distorted into a vertebral pattern at the nozzle under the action of the high-voltage electrostatic field. When the electrostatic repulsion of the droplets is greater than the surface tension, the spinning solution is rapidly ejected, and eventually a polymer jet is formed. During the stretching and movement, the solvent evaporates, and the polymer jet diameter gradually decreases and solidifies. Finally, nanofibers with the desired shape are formed and deposited on the collector.

Nanofibers with different microstructures and properties can be obtained by adjusting the intrinsic characteristics of the spinning solution (e.g. polymer molecular weight, concentration, solvent), regulating the electrospinning process parameters (e.g. spinning rate, voltage, nozzle diameter), and changing the surrounding environmental factors (e.g. temperature, relative humidity). Electrospinning technology has good operability for the preparation of nanostructured fibers. The properties are inherently like those of polymer fiber webs, including large surface-area-to-volume ratio, flexibility, lightweight, stretchability, and ductility. Therefore, electrospinning technology has a wide range of application prospects in the fields of biomedicine, filtration materials, and protective clothing [63–65].

Although electrospinning and nanofibers have many advantages, the low preparation efficiency seriously limits their industrial application. In recent years, needle-free electrospinning and melt differential electrospinning techniques have been developed to improve the preparation efficiency of nanofibers (Fig. 4b and c) [61,62]. However, further improvements in spinning stability are needed before these technologies can be industrialized.

2.4. Centrifugal spinning

Centrifugal spinning is another common method for preparing nanofibers. In 1924, Hooper filed a patent for the fabrication of nanofibers by centrifugal method [66]. In 1990, a patent was filed in the U.S.

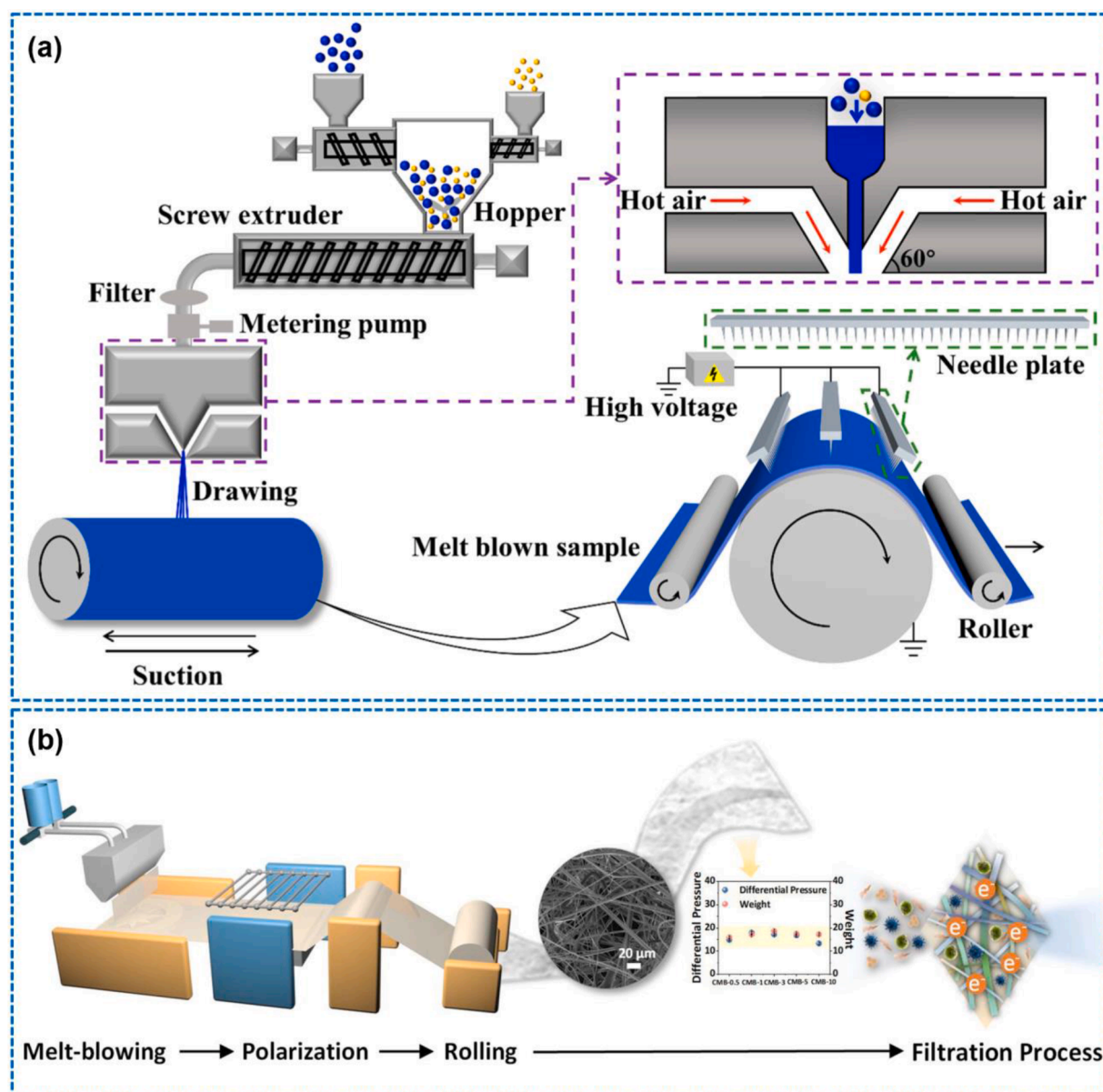


Fig. 3. Preparation of nonwovens with melt-blown technology. (a) Schematic diagram of a typical melt-blown device. (b) Fabrication process, microstructure, and filtration properties of the bicomponent polypropylene/polyvinylidene fluoride-trifluoroethylene (PP/P(VDF-TrFE)) micro/nanofiber nonwoven. Reproduced with permission from (a) Ref. [23]. Copyright 2021 MDPI; (b) Ref. [42]. Copyright 2022 American Chemical Society.

for a spinneret capable of producing fibers with different morphologies [67]. FibeRio corporation produced laboratory-grade and industrial-grade centrifugal spinning equipment using U.S. patent US2009/0289324A1 in 2009 [68]. Since then, centrifugal spinning has attracted more and more attention as an efficient method for the preparation of micro/nanofibers.

Centrifugal spinning is a method of preparing fibrous materials by drawing polymer melts or solutions by centrifugal force. Typical centrifugal spinning equipment consists of a spinneret, a shaft, a motor, and a collector (Fig. 5a) [69]. The forming process of centrifugal spun fibers can be roughly divided into three stages: (1) The polymer melt or solution is moved from the center of the spinneret to the spinneret hole under the action of centrifugal force. (2) When the centrifugal force exceeds the surface tension, the spinning melt or solution forms polymer jets. (3) These polymer jets are further drawn and refined by centrifugal force, resulting in nanofibrous material on the collector.

With the continuous improvement of centrifugal spinning technology, in addition to the conventional centrifugal spinning equipment,

some innovative centrifugal spinning equipment that combines centrifugal field with other external fields have also been developed, such as solution centrifugal electrospinning equipment, melt centrifugal electrospinning equipment, and airflow-assisted melt centrifugal spinning equipment [34,72,73]. Generally, the fiber diameter obtained by centrifugal spinning with polymer solution is smaller than that obtained by centrifugal spinning with a polymer melt. For example, the diameter of PLA fibers obtained by solution centrifugation spinning can be as low as 66 nm, while the diameter of the fibers obtained by melt centrifugation spinning is usually at the micron level (Fig. 5b and c) [70,71].

Adjusting the technological parameters of centrifugal spinning (e.g., centrifugal rate, nozzle size, nozzle-collector distance, spinning temperature) and changing the parameters of spinning melt or solution (e.g., spinning solution concentration, solvent type, polymer molecular weight, viscosity) are two main strategies for regulating the structures and properties of centrifugal spun fibers [17]. For solution centrifugal spinning, the concentration of spinning solutions has an important effect on the structure and size of fiber materials. Either too high or too low a

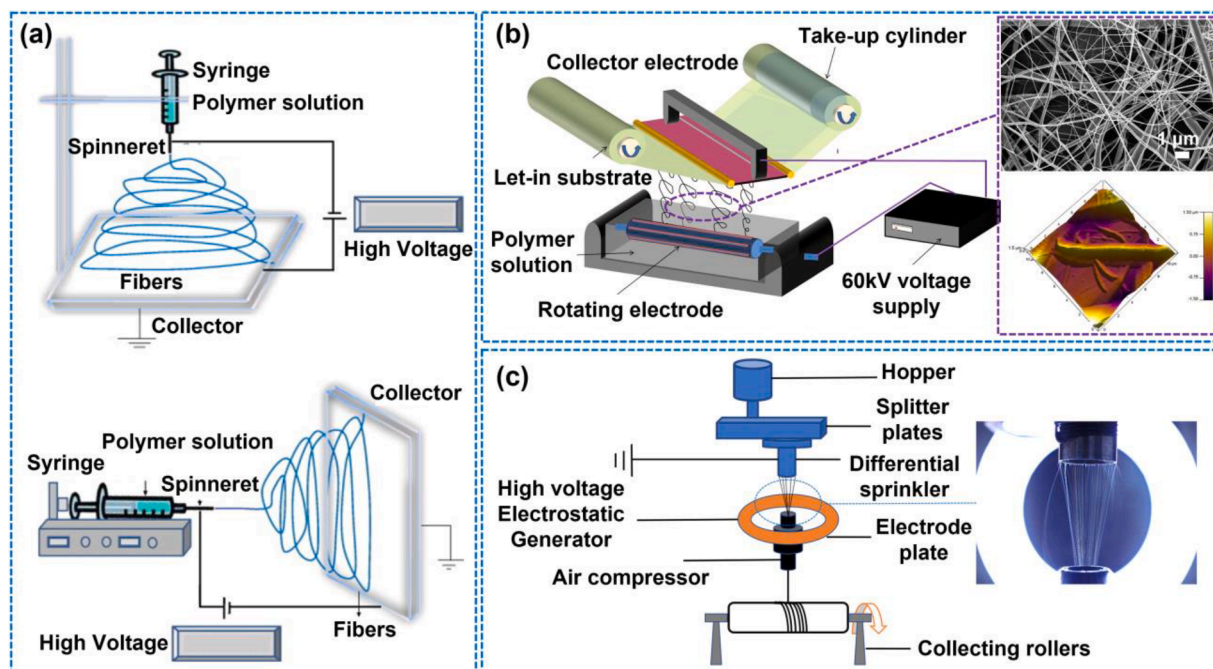


Fig. 4. Preparation of nonwovens with electrospinning. Schematic diagram of (a) the typical electrospinning devices with vertical setup and horizontal setup. (b) Schematic of needleless electrospinning device and the morphology of the resultant fibers. (c) Schematic of melt differential electrospinning device. Reproduced with permission from (a) Ref. [60]. Copyright 2010 Elsevier B.V.; (b) Ref. [61]. Copyright 2021 Elsevier B.V.; (c) Ref. [62]. Copyright 2020 Society of Plastics Engineers.

concentration of spinning solutions cannot produce fibers by centrifugal spinning [74]. Therefore, the concentration of spinning solutions should be reasonably optimized to prepare fibers with the appropriate size and good properties.

In contrast to electrospinning, centrifugal spinning can produce fiber materials from both conductive and non-conductive polymers [75]. Fiber materials with oriented structures can be easily obtained by centrifugal spinning technique because the polymer jets are drawn in the same direction by centrifugal force [76]. Despite the advantages of centrifugal spinning, the fiber materials produced by centrifugal spinning are less homogeneous than that produced by electrospinning. In addition, the high centrifugal speed of centrifugal spinning requires the higher performance of equipment components, such as motors and bearings, etc.

2.5. Solution blow spinning

Solution blow spinning, a new spinning process emerging in recent years, is gradually becoming a focus of attention due to its high yield, short preparation time, fast spinning speed, and wide selection of materials. This spinning method was first proposed by Mederios in 2009 and combined electrospinning with melt-blown technology to prepare nanofibers [77]. The earliest fiber materials prepared by solution blow spinning include polylactic acid (PLA) and polystyrene (PS) nanofibers. The effects of processing parameters on the morphology of polymer fibers by solution blow spinning were investigated, which laid the foundation for the development of solution blow spinning technology.

Solution blow spinning device mainly consists of compressed gas, injection pump, nozzle, and collector (Fig. 6a) [77]. The preparation of nanofibers by solution blow spinning is mainly based on the high-speed draft and the Bernoulli principle [78]. Polymers are first dissolved in a volatile solvent to form a homogeneous spinning solution. The spinning solution is supplied to the nozzle by an injection pump, and a Taylor cone is formed at the nozzle under the action of high-speed airflow. Polymer jets form when the shear force generated by the high-speed airflow exceeds the surface tension of the spinning solution (Fig. 6b) [77]. In the process of the jet moving towards the collector, the solvent

gradually volatilizes, the fiber solidifies, and finally, the nanofibers are obtained on the collector.

For solution blow spinning, the concentration of spinning solution has an important effect on the morphology and diameter of fiber materials. With the increase of the concentration of the spinning solution, the diameter of the fiber gradually increases, and the cross-section of the nanofibers is usually uniform and round [80,81]. In addition, the viscosity and surface tension of the spinning solution, as well as the spinning process parameters, such as airflow velocity and liquid supply velocity, also affect the final morphology of the fiber materials [82–84].

Compared with electrospinning, solution blow spinning technology does not require high voltage electrostatic field support, so it is safer and less demanding on the device. In addition, a variety of additives can be added to the spinning solution without affecting the effect of solution blow spinning. Compared with melt-blown technology, solution blow spinning can be applied to a wider range of materials. Some polymers that are not suitable for melt-blown technology can be prepared into nanofibers by solution blow spinning. In addition, since solution blow spinning uses compressed gas to prepare fibrous materials at room temperature, thermal degradation of the polymers can be effectively avoided.

Solution blow spinning can be used to prepare nanofibers with different structures, such as hollow nanofibers, nanofiber coatings, nonwovens, sponges, etc., and these materials have been widely applied in various fields, including high-temperature thermal insulation, air filtration, water treatment, flexible electronic devices, and biomedical applications [19,30,85–89]. Unlike the fibers produced by electrospinning, the solution blow spun fibers have no electrostatic repulsion between them, so fiber bundles are easily formed. Bunches of fibers can cause uneven fiber distribution, thus affecting the application of fibrous materials in some fields, such as air filtration [30]. Similar to electrospinning, needleless solution blow spinning and multi-needle solution blow spinning have been developed to improve the efficiency of fiber preparation (Fig. 6c–e) [29,79].

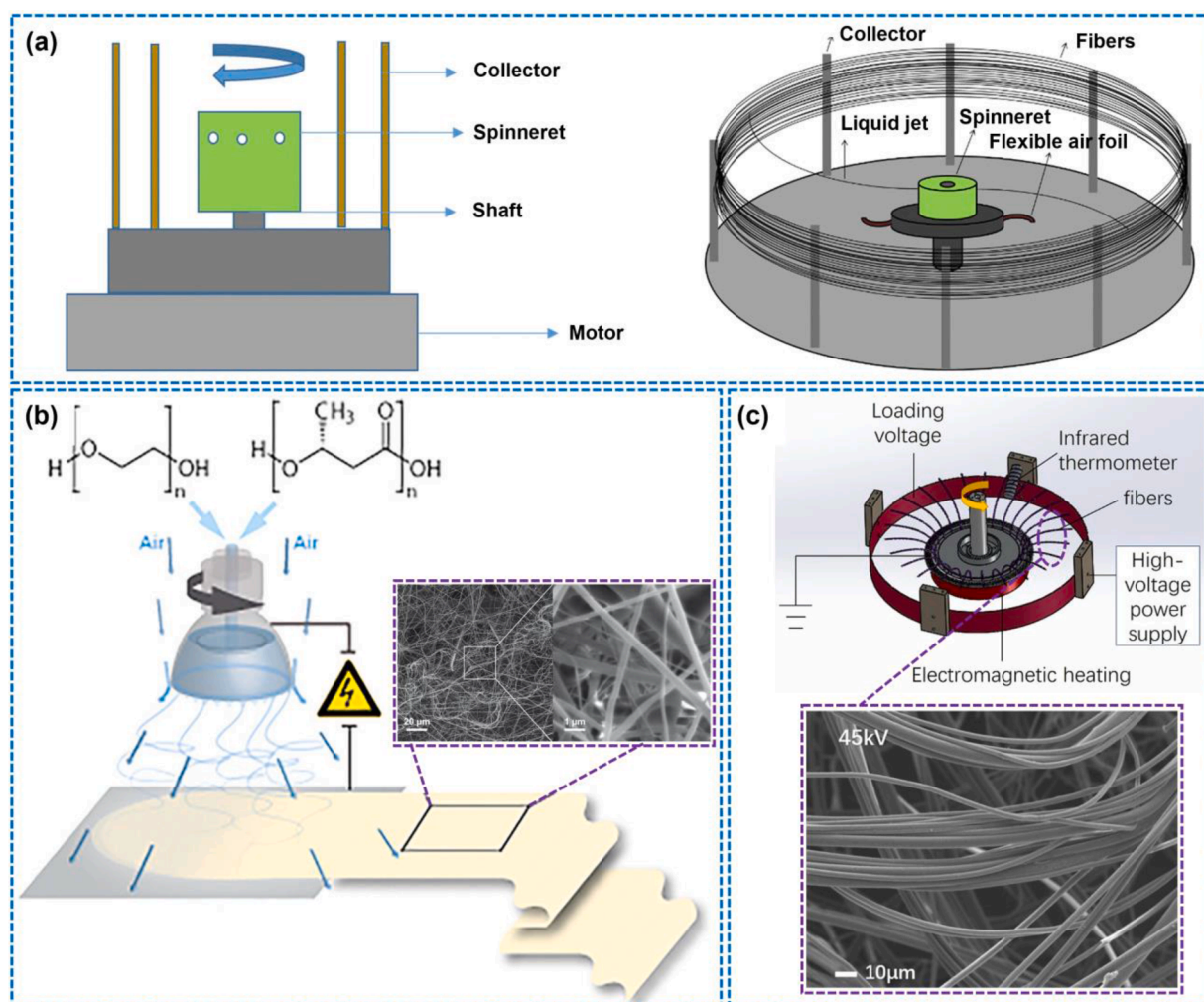


Fig. 5. Preparation of nonwovens with centrifugal spinning. (a) Schematic of a typical centrifugal spinning device. (b) Schematic of the solution centrifugal electrospinning device and morphology of the nanofiber nonwoven. (c) Schematic of the needleless centrifugal electrospinning device and morphology of the microfibers. Reproduced with permission from (a) Ref. [69]. Copyright 2019 Springer Nature; (b) Ref. [70]. Copyright 2020 American Chemical Society; (c) Ref. [71]. Copyright 2019 John Wiley and Sons.

2.6. Flash spinning

Flash spinning technology is a process for producing micro/nanofibers or filamentary products directly from polymer spinning solutions. This technology is based on the principle of phase separation and supersonic flow to prepare micro/nanofibers [90]. Dupont first developed and applied for the patent of flash spinning technology in 1966 [91], and continuously improved and innovated the technology for a long time [92,93].

Flash spinning equipment mainly consists of four parts: an autoclave, a spinneret, a collector, and a high-speed airflow or electrostatic generator (Fig. 7) [20]. First, polymers are dissolved in suitable solvents under high temperature and pressure to produce a spinning solution. The spinning solution is mainly composed of polymers, primary solvent, secondary solvent, and additives [94]. Then the spinning solution spurts out from the spinneret of the autoclave instantly, and the solvents evaporate rapidly due to the sudden pressure drop. The polymers are solidified and stretched to form ultrafine fibers by high-speed airflow. Generally, additional high-speed airflow or high-voltage electrostatic field is used to unwrap the bundle of fibers.

Different from other spinning methods, flash spinning usually uses insoluble polymers to prepare fiber materials. The resulting fiber materials have high strength, excellent puncture and tear resistance, good barrier property, excellent water resistance, and air permeability.

Because of these excellent properties, flash-spun fiber materials have a broad application prospect in the fields of air filtration and medical protection materials [95,96]. In particular, the protective clothing prepared with these fiber materials has good comfort, excellent mechanical properties, and superior barrier performance to a variety of pathogenic microorganisms and liquids.

3. Properties of medical protective fiber materials

From the COVID-19 outbreak in 2020 to the present, the global demand for PPE has increased significantly. The wearing and selection of PPE need to be based on the surrounding contamination and risk level. Three approaches are typically used to evaluate the selection of PPE: test methodologies, product or property specifications, and technical reports or advice materials. In addition, PPE is generally required to have good liquid and particle barrier properties, breathable properties, and mechanical properties [97]. Recently, micro/nanofiber nonwoven protective materials with high abrasion resistance, high breathability, and high barrier property have received wide attention [98–100]. In this section, we briefly described the barrier properties, comfort properties, and mechanical properties of micro/nanofiber nonwoven as PPE.

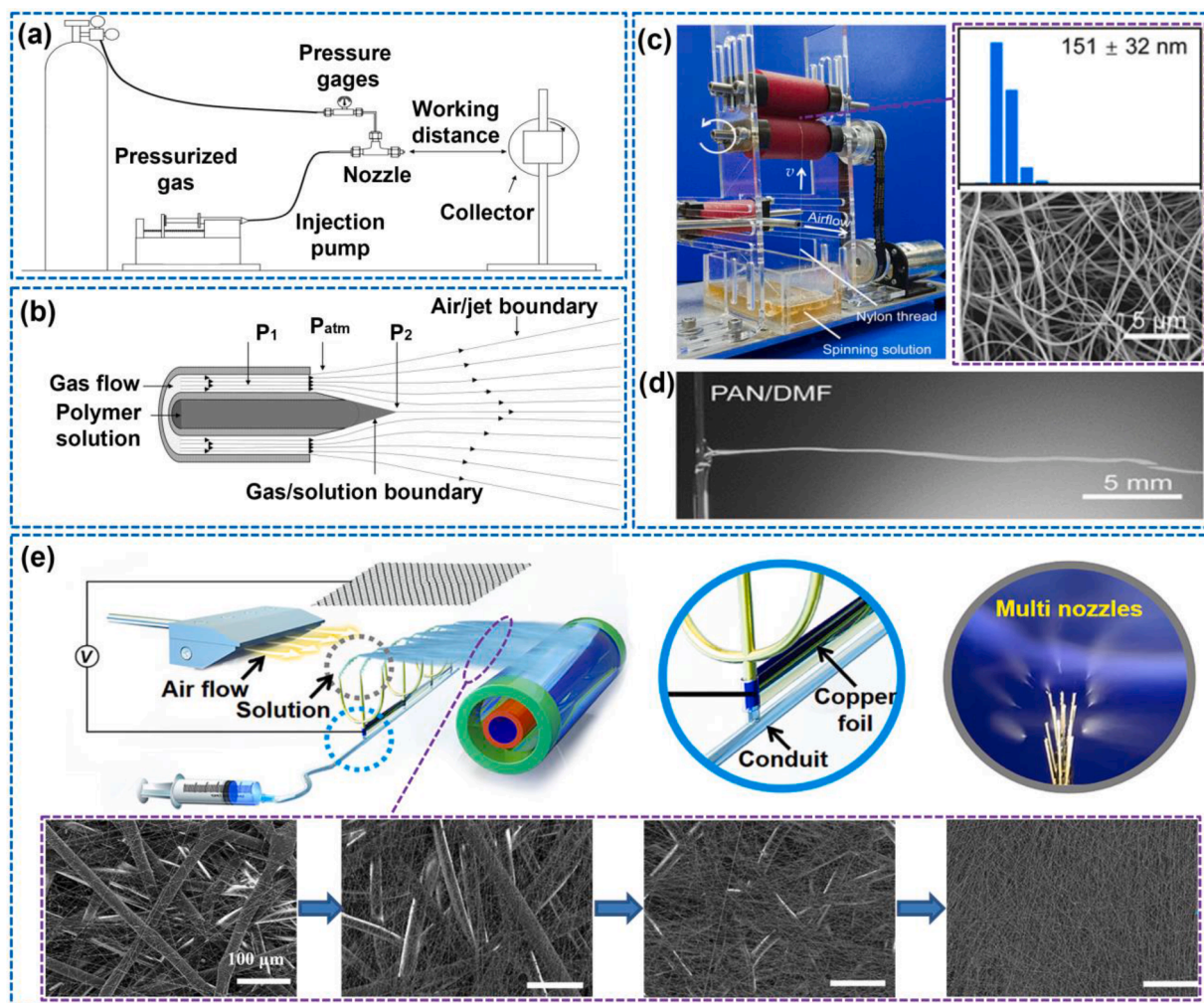


Fig. 6. Preparation of nonwovens with solution blow spinning. (a) Schematic of a typical solution blow spinning apparatus. (b) Schematic showing the mechanism of needleless solution blow spinning. (c) Digital image of a needleless solution blow spinning device and the morphology of the nanofibers with a diameter of 151 nm. (d) High-speed camera image of a needleless solution blow spinning jet. (e) Schematic of multi-needle electro-blow spinning and SEM images of the prepared fiber materials. Reproduced with permission from (a-b) Ref. [77]. Copyright 2009 John Wiley and Sons; (c-d) Ref. [29]. Copyright 2022 AAAS; (e) Ref. [79]. Copyright 2022 American Chemical Society.

3.1. Barrier properties

Pathogens can be transmitted using body fluids, dust, and aerosols as carriers. Therefore, PPE with functional characteristics such as liquid and solid particle barriers are extremely important for healthcare applications. Depending on the potential medical environment, testing items for PPE include water resistance (hydrostatic pressure, impact penetration), synthetic blood penetration resistance, virus penetration resistance, dry (wet) microbial resistance, microbial aerosol resistance, and particulate filtration property [101]. The barrier properties of PPE can protect medical personnel and individuals from being infected by blood-borne pathogenic bacteria or solid particles, and the main evaluation criteria include liquid barrier assessment and aerosol barrier assessment.

Liquid barrier. The wettability and permeability of micro/nanofiber nonwoven materials are important indicators for assessing the liquid barrier property of PPE [102]. According to the requirement of infiltration equilibrium theory, the liquid should present a water droplet shape on the surface of nonwoven materials, that is, the contact angle between nonwoven materials and liquid is in the range of 90° – 180° . At the same time, the surface tension of hydrophobic micro/nanofiber nonwoven materials should be smaller than that of liquid as much as possible. Modification of nonwoven materials is needed to meet these

two requirements. In other words, to improve the liquid barrier property of PPE, liquid-repellent finishing of nonwoven materials is required [103]. The surface treatment of nonwoven materials with fluorinated finishing agents can effectively improve their filtration, breathability, and liquid barrier properties [104]. High-density polyethylene (PE) nonwoven materials manufactured by flash spinning has a dense structure, smooth surface, and high hydrophobicity, and has become an ideal material for making high-performance protective clothing [95].

Aerosol barrier. Aerosols are systems of air masses formed by liquid or solid particles suspended in a gaseous medium. Since aerosols are one of the main ways for transmission of the COVID-19 virus, PPE is required to have good aerosol barrier properties [105]. The aerosol barrier can be divided into two categories, namely, surface protection and an internal interception. Surface protection comes in three forms: (1) mechanical interception, that is, particles with a diameter larger than the pore size of the fiber network can be intercepted; (2) electrostatic adsorption, the adsorption effect is affected by the electrical properties of fibers; (3) bridging interception, particles are intercepted outside the pores due to factors such as adsorption or aggregation [106]. Internal interception means that particles with small diameters are blocked and retained inside the fiber materials after hitting the fibers at a certain speed. Nonwoven materials manufactured by electrospinning, solution blow spinning, and flash spinning have an irregular three-dimensional

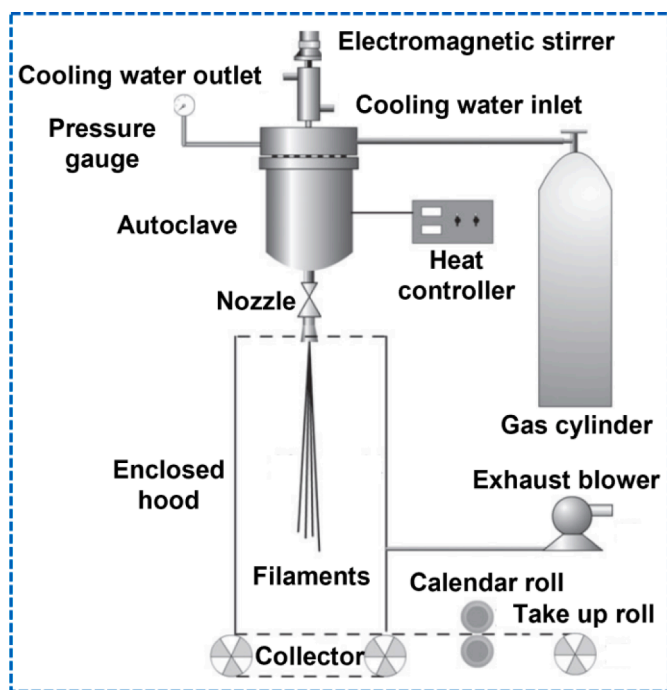


Fig. 7. Schematic diagram of a typical flash spinning apparatus. Reproduced with permission from Ref. [20]. Copyright 2016 De Gruyter.

network structure with small fiber diameters and high porosity, resulting in their high permeability and high barrier property to aerosols [107, 108].

3.2. Comfort

In order to obtain high-safety PPE, some methods have been adopted to improve the barrier properties of nonwoven materials, such as coating, lamination, plastic film covering, etc. [109,110]. However, these treatments inevitably reduce the comfort of PPE. About 85% of the body's heat is emitted through the skin, so the permeability is an important indicator for protective clothing. When a person moves around in a relatively enclosed space, the rate of sweating will be greatly increased, which will lead to the poor comfort of protective clothing [111]. Therefore, it is an important research direction to develop nonwoven materials with excellent moisture permeability and breathability.

Some advanced techniques have been used to improve the permeability and breathability of nonwoven materials. For example, latent heat materials can be used to improve the temperature regulation ability of nonwoven materials, so as to keep the human body in the normal comfort range [112]. In addition, a water-resistant breathable film sandwiched between two layers of nonwovens enables water vapor to be discharged through nonwoven materials while liquids and pathogens cannot enter the interior through them [113]. Another innovative approach is to design nonwoven materials with unidirectional wettability properties, allowing heat and moisture generated by the body to be efficiently transferred out [114,115]. This method realizes the unidirectional wettability of nonwoven materials by changing the fiber linear density, hydrophilicity, and fiber network structure, and using differential capillary effect and wetting gradient effect. All these methods can effectively improve the comfort of medical protective clothing.

At present, the commonly used raw materials of nonwoven protective clothing are PP, PE, and PET. The surface of these nonwoven materials is chemically inert and will generate static electricity after contact with the body, thus affecting the comfort of protective clothing. Several

strategies have been used to improve the antistatic properties of nonwoven materials, including coating the surface of the nonwoven antistatic agent, adding hydrophilic components to improve the hygroscopic properties, and adding conductive components in the fibers [116, 117]. In addition, the surface of PP fibers treated with argon plasma and grafted with acrylic acid can also effectively improve the hygroscopic and antistatic properties of nonwoven materials [118].

3.3. Mechanical properties

The mechanical properties of nonwoven materials used in PPE have an important influence on their wearable and protective properties [119]. PPE needs to maintain adequate mechanical properties throughout its life cycle. The micro/nanofiber materials obtained by most spinning technologies have certain limitations when used in PPE manufacturing. For example, fibers prepared by spun-bonded technology typically have diameters ranging from 15 to 40 μm , and although these fibers have excellent tensile strength and wear resistance, their barrier properties are poor. In contrast, fibers prepared by electrospinning, melt blowing, and solution blow spinning, can effectively block liquids and particles, but their mechanical properties are poor. It should be emphasized that the micro/nanofiber materials prepared by flash spinning method with PE as raw material show excellent mechanical properties and barrier properties.

In order to make PPE have excellent mechanical properties and barrier properties, a common method is to combine fibers with good mechanical properties prepared by spun-bonded technology and fibers with good barrier properties prepared by melt-blown technology to make spun-bonded/melt-blown/spun-bonded (SMS) structure [120]. The SMS structure makes full use of the advantages of fibers obtained by different spinning methods. Based on this idea, the breathable microporous membrane made of polytetrafluoroethylene (PTFE), PE, and thermoplastic polyurethane (TPU) can be laminated with micro/nanofiber nonwovens to obtain a sandwich structured material with good tensile strength, filtration property, hydrostatic pressure resistance and breathability [121,122].

4. Applications of medical protective fiber materials

Since the global outbreak of COVID-19 in 2020, the World Health Organization has proposed a variety of effective measures to stop the spread of the coronavirus, including community containment, travel restrictions, social distancing, quarantine, and the use of PPE [6]. Of these measures, wearing PPE is the one that has the least impact on people's lives. There are various types of PPE, including scrub caps, masks, gloves, protective clothing, and shoe covers [123]. In order to achieve effective protection, the appropriate PPE needs to be selected, and the following three aspects should be considered: (1) the type of liquid and size of particulate matter to which the wearer may be exposed; (2) the durability and comfort of the PPE; and (3) the suitability of the PPE for the individual user [124]. In this section, we introduced PPE for different parts of the human body in detail, focusing on masks, protective clothing, etc.

4.1. Masks

Masks have become an important part of people's lives during the COVID-19 pandemic. Not only do masks barrier liquids and aerosols with viruses and reduce the risk of infection, but they also filter air and provide good breathability. A wide range of masks are available on the market and can be broadly classified as cotton masks, surgical masks, and respiratory masks [125]. Cotton masks are made of one or more layers of ordinary cotton fabric and are usually only used for very low-risk protection. In terms of breathability and comfort, cotton masks are often more comfortable than micro/nanofiber nonwoven masks.

Surgical masks are usually fabricated from three layers of the

nonwoven fabric of SMS structure (Fig. 8a) [126]. The outermost layer (cover layer) of the mask is a hydrophobic, spun-bonded nonwoven that keeps out fluids and particles. The middle layer (filter layer) is a layer of melt-blown nonwoven used to filter aerosols or particles. The micro/nanofibers of melt-blown nonwovens have a very small diameter of about 1 μm , which provides an efficient liquid barrier and particle trapping properties (Fig. 8b and c). Commercially available melt-blown micro/nanofiber nonwovens are mainly based on PP [127], and electrostatic electret treatment of melt-blown PP nonwovens can effectively improve their filtration properties (Fig. 8d) [128,129]. The inner layer (shell layer) is also a spun-bonded nonwoven, which is used to absorb the moisture from the wearer. Although surgical masks can effectively block liquids and large particles, they have poor barrier performance to ultra-small particles and other nanoscale pollutants (less than 0.3 μm), such as influenza virus [130,131]. Another disadvantage of surgical masks is that they do not fit tightly to the human face, allowing air to enter the inside of the mask from both sides, increasing the risk of virus infection for the wearer.

Respiratory masks consist of four layers, namely an inner layer, a support layer, a filter layer, and an outer layer (Fig. 9a) [132]. The outer layer is a hydrophobic PP micro/nanofiber nonwoven that resists external liquids. The filter layer is made of double-layer melt-blown PP nonwoven for blocking particulate matter. The support layer is manufactured from modacrylic fibers to improve the thickness, rigidity, and comfort of the mask. The innermost layer is also made of hydrophobic PP nonwoven to resist moisture inside the mask, thus maintaining the filtration property of the mask.

The respirator masks are more tightly fitted to the wearer's face, thus preventing fluids, particles, and microorganisms. The filtration efficiency of these masks is more than 95% for ultra-small particles smaller than 0.3 μm , which can effectively protect doctors, medical personnel, and industrial workers (Fig. 9b and c). There are many kinds of respirator masks on the market, such as N95 (United States), FFP2 and FFP4 (European), KN95 (China), P2 (Australia/New Zealand), Korean Class1 (Korea), and DS (Japan) [133]. A study conducted by physicians at the Zhongnan Hospital of Wuhan University showed that none of the 278 physicians wearing N95 masks were infected with the coronavirus, while 10 of the 213 physicians not wearing N95 masks were infected with coronavirus [134].

4.2. Protective clothing

Personal protective clothing is usually made of impermeable textiles

and coating, which can effectively block outside substances, thus providing good protection. However, the large size, heavy weight, and poor air permeability of these protective suits make the wearer very uncomfortable [135]. Protective clothing based on micro/nanofiber nonwoven has received widespread attention for providing good barrier performance while maintaining comfort and breathability, in addition to the low price of raw materials. Micro/nanofibers have a large surface area to volume ratio, which allows them to filter particles and increase hydrophobicity. The micro/nanoscale pores in nonwovens can make air and water vapor pass through, while liquids and particles are blocked. Liquid resistance and breathability can be effectively improved by adjusting the porous structure and porosity of nonwovens. For example, reducing the pore size in nonwovens can effectively block liquid entry and improve the barrier performance, while increasing the porosity of nonwovens can increase gas transmission, thereby improving the breathability [136].

Medical protective clothing is a sort of protective clothing that protects the wearer from infection with harmful liquids and solids, and they can also prevent pathogens from attacking patients with low immune systems. Medical protective clothing can be divided into disposable protective clothing and reusable protective clothing [137]. Reusable medical protective clothing is usually made of fabrics with a tight plain structure, and they can be treated through a pad-dry-cure technique to enhance the barrier properties. Reusable protective clothing is required to be able to repeat the wash and dry cycle at least 50 times [138]. However, this type of protective clothing can wear out during wearing, and multiple washing processes can cause the fabric to decompose and damage, thus reducing its barrier performance.

Disposable medical protective clothing is typically made from micro/nanofiber nonwovens (e.g. PP, PET, and PE) with a surface density of 30–45 g/m^2 [139]. The nonwovens with desired properties can be obtained by choosing the appropriate fiber type, adhesion technology, and nonwoven finishing method. Disposable protective clothing not only has excellent liquid and microbial barrier properties but also maintains good breathability and comfort, which has become the preferred choice of medical staff [140,141].

4.3. Other PPE

Other common PPE include scrub caps, gloves, and shoe covers. The scrub caps are produced from cotton, PET, PP, and other fiber materials, and they can be used to protect the wearer's head and hair from contamination by pathogenic microorganisms and other liquids [133].

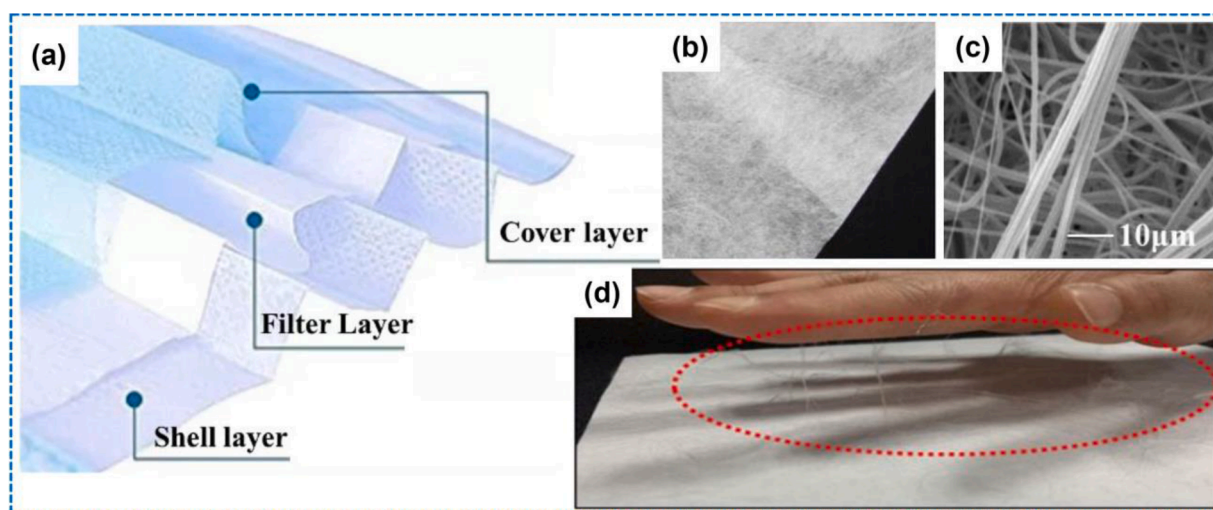


Fig. 8. (a) Schematic diagram of the different structural layers of a typical surgical mask. (b) Digital image of the filter layer in a surgical mask. (c) SEM image of the micro/nanofibers of the filter layer. (d) Digital image showing the electrostatic adsorption of the filter layer. Reproduced with permission from (a–c) Ref. [126]. Copyright 2020 Elsevier B.V. and (d) Ref. [129]. Copyright 2020 American Chemical Society.

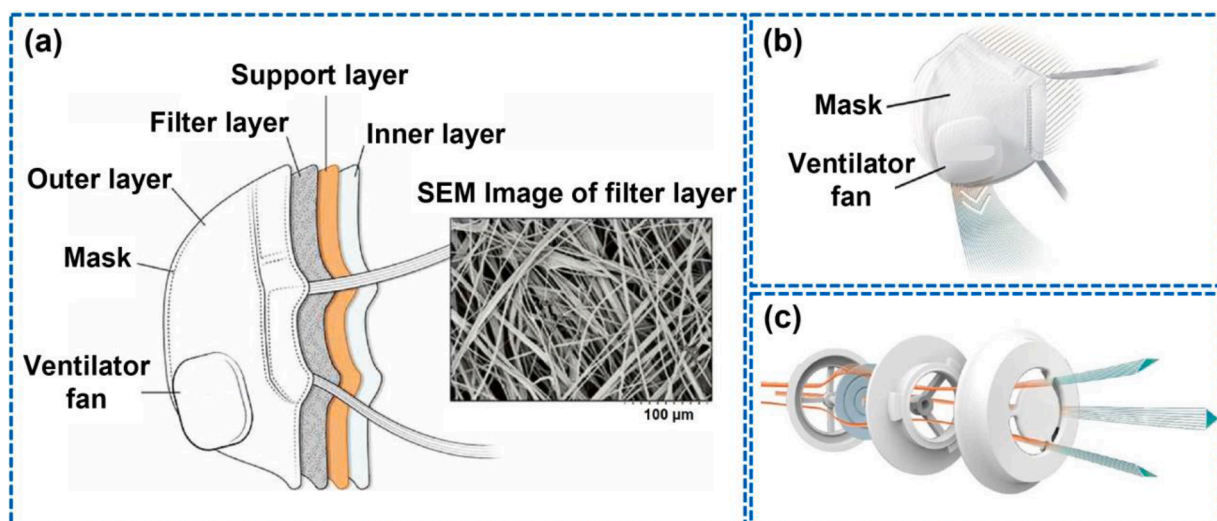


Fig. 9. (a) Schematic showing the structures of a typical respiratory mask. Inset is the SEM image of the filter layer. (b) Schematic of a respiratory mask with ventilator fan. (c) Schematic diagram of working principle of ventilator fan. Reproduced with permission from Ref. [132]. Copyright 2018 AME Publishing Co.

In addition, the scrub caps also can prevent the hair from blocking the view of the wearers. The scrub caps made of nonwovens have a good protective effect and excellent air permeability, making the wearer more comfortable to wear [123]. Medical shoe covers can effectively protect the foot and ankle from stains and foreign substances and can prevent blood or other fluids from seeping inside the shoes. These covers are generally manufactured using heavier nonwoven than regular shoe covers, offering the advantages of being strong, soft, comfortable, and safe [142].

Disposable gloves are made from PET and PP fibers. Sometimes different co-blended or composite fibers are also used to make

disposable gloves, which are intended to serve as protection for medical workers from viral contamination during patient treatment. Micro/nanofiber nonwoven disposable gloves have been approved to effectively prevent direct contact of contaminants with medical workers [143].

5. Current and future development trend of medical protective fiber materials

At present, although effective therapeutic drugs and preventive vaccines have been successfully developed in response to COVID-19,

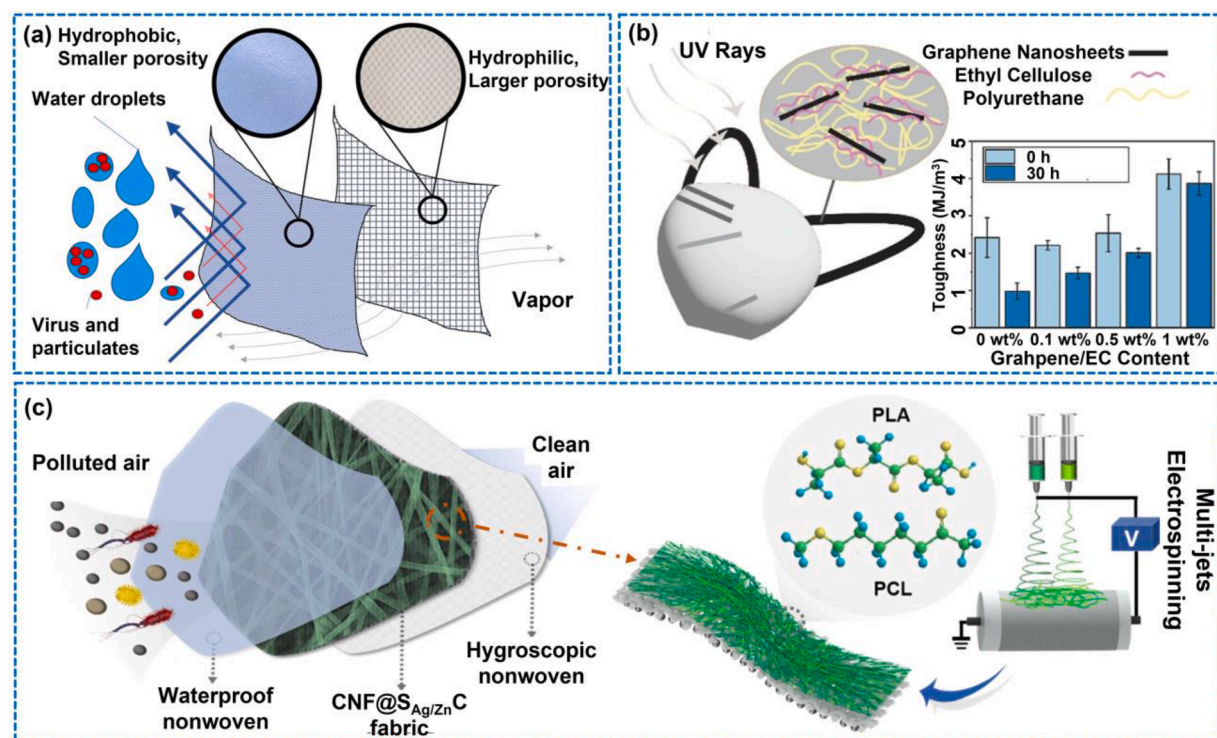


Fig. 10. Reusable and bio-based medical protective fibers. (a) Schematic of the preferred Janus fabrics with layered structures. (b) Schematic of graphene/EC anti-UV additive improving property of PU masks, and the property changes before and after UV irradiation. (c) Schematic of environmental-friendly and antimicrobial bilayer structured PPM for filtration of PMs. Reproduced with permission from (a-b) Ref. [146,147]. Copyright 2022 American Chemical Society and (c-d) Ref. [26]. Copyright 2022 Elsevier B.V.

wearing PPE is still one of the main means to block the spread of the virus [144]. In order to achieve high safety and comfort of PPE, and to meet the needs of human response to major public health events and environmental protection, the development of new medical protective fiber materials is still an important direction.

5.1. Reusable and bio-based medical protective fibers

Nowadays, disposable PPE is still mainly manufactured from petroleum-derived polymers, such as PP, PE, and PET. The high consumption of these petroleum-derived polymer raw materials puts a huge pressure on the environment and economic cost. In addition, the used disposable PPE is disposed of by incineration or landfill, which brings secondary harm to the surrounding ecological environment and human health [145].

The use of reusable PPE can replace disposable PPE to reduce the ecological pollution of medical waste. Yang et al. developed sustainable, durable, and high-performance protective fabrics and evaluated their filtration property, morphology, wetting behavior, and washing resistance (Fig. 10a) [146]. The morphology and wetting behavior of the fibers play an important role in breathability, filtration efficiency and durability. Hydrophobic fabrics with smaller porosity exhibit higher filtration efficiency because they can intercept aerogels as well as prevent liquid penetration, while hydrophilic fabrics with larger porosity are more breathable. The combination of these two fabric layers can effectively improve the materials' tear and wear resistance, and make them withstand chemical changes during washing.

Ultraviolet (UV)-irradiation sterilization is an effective method to improve the reusability of masks. However, this method can damage the toughness of the masks, and thus weaken the protective property. Kuo et al. added graphene/ethyl cellulose (EC) in polyurethane (PU) masks to improve their UV-radiation resistance (Fig. 10b) [147]. Graphene/EC can absorb UV light and inhibit photo-induced degradation of the PU matrix. In addition, the anti-UV additive can improve the mechanical properties of PU, and the PU masks after 150 UV-irradiation sterilization treatment still maintain good mechanical toughness. Although the reusable PPE can replace disposable PPE to some extent, the recycling and disinfection of these products are time-consuming and costly [148].

The development of medical protective fiber materials using bio-based polymers, such as PLA and cellulose, can significantly reduce the environmental impact of waste PPE [149,150]. Cheng et al. developed an environmentally friendly high-performance bilayer personal protective mask (PPM) fabric by combining Ag/Zn sputtered cotton and biodegradable PLA/PCL composite nanofibers (Fig. 10c) [26]. As the core intermediate layer of PPM, the bimolecular layer fabric exhibits high antibacterial activity and 99% filtration efficiency to PM_{0.3}, and is harmless to human body. This work provides a new perspective for the development of high-performance filter media.

5.2. Antibacterial/antiviral medical protection fibers

The existing medical protective fiber materials can only achieve the protective effect by blocking pathogenic microorganisms, but cannot actively inactivate them. Although pathogens can be blocked on the surface or inside the PPE, secondary infection can easily occur if the wearer's hands or other body parts come into contact with the contaminated PPE or if the PPE is not handled properly [151]. Disinfection and cleaning of these contaminated PPE can effectively reduce the risk of secondary transmission of the virus, but contact between the human body and PPE is still difficult to avoid.

The active protective function of medical protective fibers can be realized by adding antibacterial/antiviral materials in fibers or coating them on the surface of fibers [62,152–154]. Metal oxides have been shown to have excellent antibacterial and antiviral properties. In our previous work, we designed a metal-hybrid Cu₂O@HNTs antimicrobial agent with Cu₂O immobilized *in situ* on one-dimensional inorganic

halloysite nanotubes (HNTs) [155]. With the synergistic effect of charge adsorption of metal oxides and physical perforation effect of small size nanotubes, the PET fibers containing Cu₂O@HNTs prepared by *in-situ* polymerization and melt spinning processes exhibit broad-spectrum antibacterial ability (Fig. 11a).

Cotton is one of the most common fiber materials in our daily life. It is usually treated with surface coating to endow cotton antibacterial and antiviral properties. It is very important to improve the binding strength of antibacterial materials and cotton fibers for the application of antibacterial cotton fabric. Qian et al. demonstrated a simple, cost-effective method for fabricating cotton fabrics with efficient antibacterial/antiviral properties by stably combining copper ions with hydroxyl groups on the cellulose chains (Fig. 11b–e) [156]. The modified cotton fabrics show excellent mechanical stability, and can be washed for many times. Therefore, these cotton fabrics have a great application prospect in the fields of daily use products, medical protection, medical supplies.

5.3. Visual detecting medical protective fibers

Early detection is an effective strategy to reduce bacterial/viral infections, especially in situations like the response to the current COVID-19 pandemic. Chest computed tomography (CT) imaging detection technique, nucleic acid detection technique, and immunoassay technique are currently the most commonly used methods for COVID-19 diagnosis [157]. Although these methods have suppressed the spread of the epidemic in a timely manner, there are still problems of insufficient or incorrect material during testing or sampling [158,159]. Therefore, the development of accurate, rapid, and visualized assays urgently requires more advanced materials and technologies to combat the epidemic.

The limitations of large-scale monitoring of viruses can be overcome by using nanoparticle colorimetric technology in combination with medical protective fibers. Jokerst et al. described the combination of modular substrates and gold nanoparticles for colorimetric detection of viral replication-associated proteases (M^{PrO}) (Fig. 12a) [160]. Considering the simplicity of this colorimetric assay, it can be integrated into portable point-of-care devices, including those on face masks. A sticker-based test sensing strip was fixed to the inside of the mask, and the exhaled gas was used to predict whether the person under test is infected with the virus (Fig. 12b). In principle, one pink lane and one purple lane indicate a negative result, and two purple lanes indicate a positive result for the test.

Based on the fact that metabolites produced by bacteria as they reproduce can cause changes in the pH values of their surroundings, Snari et al. prepared a reversible, sustainable, simple, biodegradable, and cost-effective biochromic fabric assay for bacterial detection [161]. A highly sensitive biochromatic indicator was used in combination with fabric to colorimetric detect pH value changes in bacterial cultures. Ammonia released during the growth of Gram-negative bacteria such as *E. coli* causes a red-purple change, while lactic acid released during the growth of Gram-positive bacteria such as *L. acidophilus* causes a red-yellow change (Fig. 12c).

5.4. Intelligent medical protective fibers

Another trend in the development of medical protective fibers is the integration of remote management and self-detection functions to develop intelligent protective fiber materials [157,162]. Smart micro/nanofiber nonwovens not only allow the wearer to self-monitor their health at home through a connected wearable device but also transmit data related to vital signs to a remote health care professional who can easily determine if the data shows early signs of illness [163]. Therefore, smart protective fibers will bring people a safer and more convenient life [164,165].

During the COVID-19 pandemic, people wearing smart medical protective equipment can not only reduce their own risk of infection but

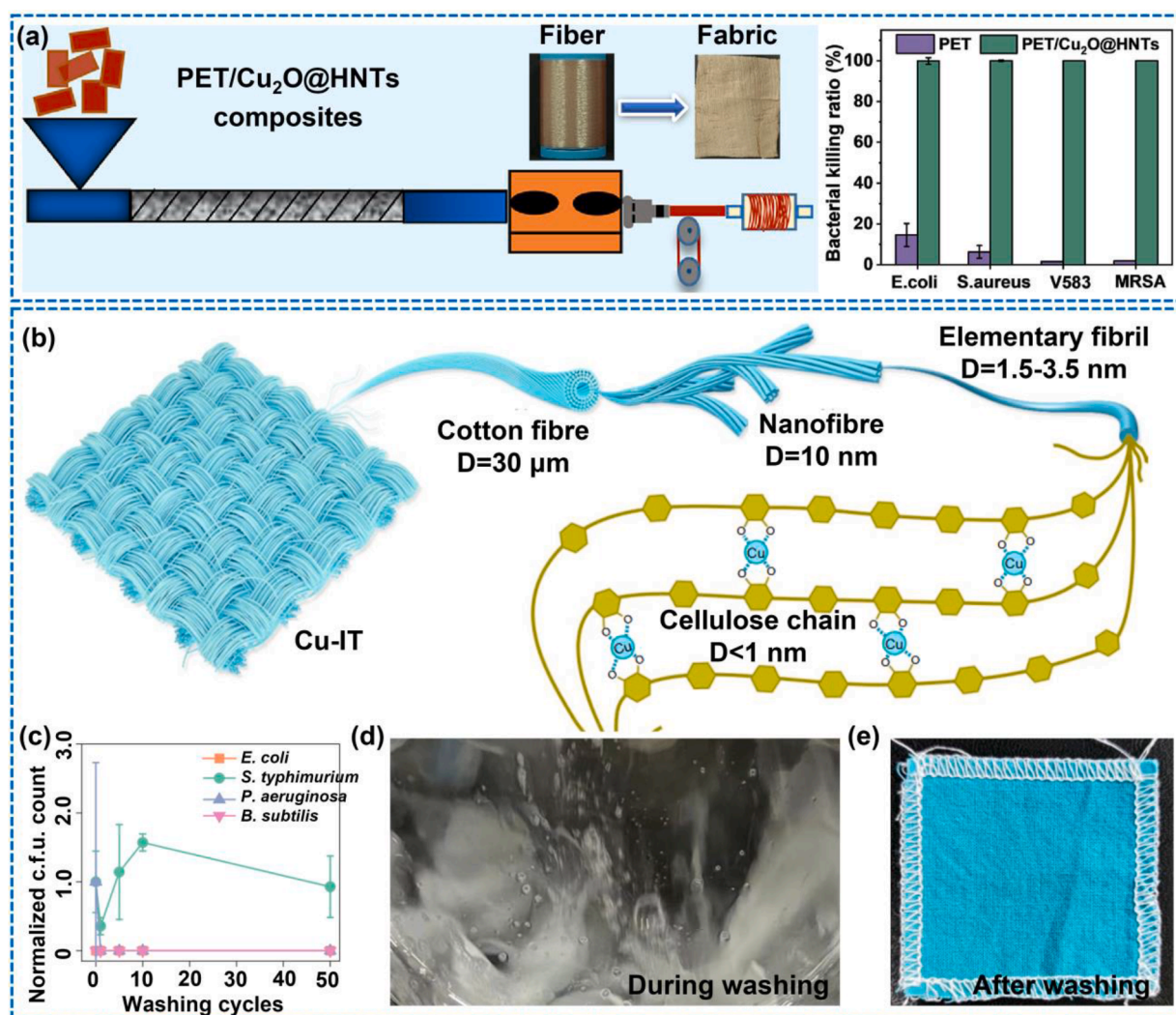


Fig. 11. Antibacterial/antiviral medical protection fibers. (a) Preparation schematic and property of melt spun PET fibers containing $\text{Cu}_2\text{O}@\text{HNTs}$ antimicrobial agents. (b) Schematic showing the structure of the copper ions modified cotton fabrics. (c) Antibacterial/antiviral properties, and (d, e) washing resistance of the modified cotton fabrics. Reproduced with permission from (a) Ref. [155]. Copyright 2022 Elsevier B.V. (b–e) Ref. [156]. Copyright 2022 Springer Nature.

also protect healthcare workers. These smart devices can track and feedback the wearer's physiological condition in real-time, and detect the health condition of the infected person, such as fever, cough, and other symptoms [166–168]. Moreover, a data algorithm for designing wearable protective equipment has been developed to detect early indications and symptoms of illness linked to the outbreak of COVID-19 [169].

6. Conclusions and outlook

Medical protective fiber materials play an important role in protecting people's lives and health, whether in response to the current COVID-19 outbreak or in preparation for the next round of unknown outbreaks. However, the development of medical protective fiber materials still needs to face the following common challenges.

The use of medical protective fibers made of bio-based polymers to replace existing medical protective fibers made of petroleum-derived polymers can reduce the ecological damage on a large scale. However, medical protective fibers made from biodegradable polymers have problems such as high cost and poor mechanical properties. In addition, choosing solvent free or low toxic solvents for processing medical protective fiber materials is also an important measure to reduce their environmental impact.

The combination technology of nanomaterials with micro/nanofiber nonwoven materials can effectively improve the protective performance of PPE, but the possible health risk of nanoparticle inhalation into the human body and the potential toxicity of the coating to the skin should be considered in the future [170]. In addition, antimicrobial nanoparticles with self-cleaning properties can only release reactive oxygen species (ROS) under sunlight to inactivate viruses or bacteria [171]. Therefore, it is necessary to develop dark-active antimicrobial nanoparticles that can release ROS even in indoor or light-free environments.

The development of specific, sensitive, portable, and rapid-response visual detection of medical protective fiber materials is critical to combat future unknown epidemic outbreaks. However, the biosafety of the required materials needs to be considered, such as the safety of specific antigens/antibodies and the cytotoxicity of chromogenic nanoprobe. In addition, the manufacturing cost of the medical protective fiber materials for visualization detection is also important for the future market promotion and feasibility.

Although intelligent medical protective fiber materials have many potential applications, some issues still need to be resolved, including design and preparation of smart micro/nanofiber nonwovens, device operation and stability, data processing, and clinical significance. In order to ensure the security of remotely collected data, access rights must be set, and data encryption must be applied. In addition, it is very

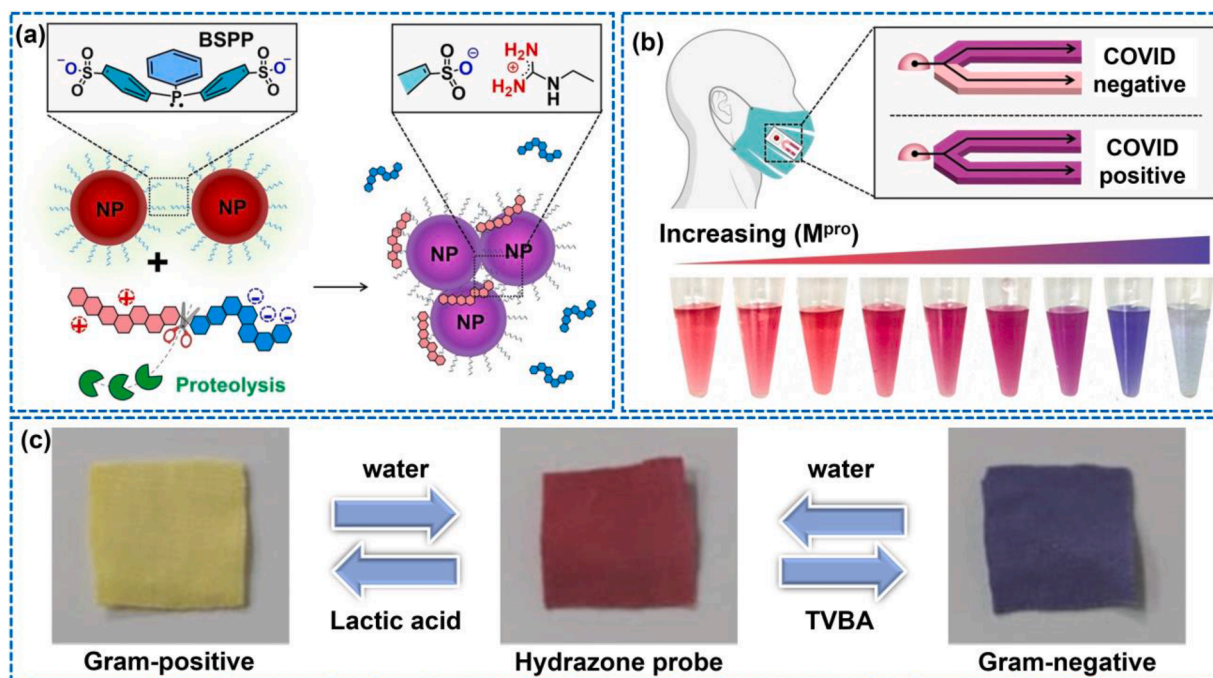


Fig. 12. Visual detecting medical protective fibers. (a) Schematic showing the colorimetric detection of viral replication-associated proteases by combining modular substrates and gold nanoparticles. (b) The colorimetric test can be coupled with face coverings with a lateral flow strip to indicate Covid infection *in situ*. (c) Digital images of the biochromic fabric assay for bacterial detection based on color changes. Reproduced with permission from (a-b) Ref. [160]. Copyright 2021 John Wiley and Sons (c) Ref. [161]. Copyright 2022 Elsevier B.V.

necessary to formulate rules and regulations for data protection.

From the preparation and functionalization of medical protective fiber materials to the development of personal protective equipment, and the disposal of waste protective materials, it involves many fields, including material science, medicine, biology, environmental science, and so on. In order to deal with the problems of medical protective fiber materials, extensive cooperation between personnel in these fields is needed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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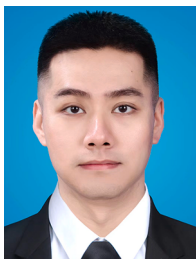
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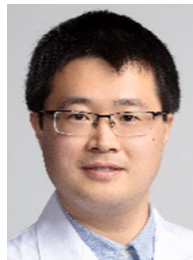
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