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Progress on fiber engineering for fabric innovation in ecological hydrophobic design and multifunctional applications

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The application of fluorinated coatings on textiles has garnered substantial research interest over the past years, owing to their ability to endow fabrics with exceptional hydrophobic characteristics, thereby mitigating issues associated with high moisture absorption and susceptibility to contamination. Nevertheless, the deployment of fluorinated substances has been proscribed due to concerns regarding their ecological impact and potential human toxicity. Consequently, there has been a burgeoning demand for hydrophobic textile alternatives derived from non-fluorinated, natural materials that are both sustainable and environmentally benign. This paper presents a thorough overview of the advancements in the development and functionalization of eco-friendly, hydrophobic textiles. Initially, the natural materials and their derivatives utilized in the creation of superhydrophobic textiles are delineated, including cellulose, lignin and chitosan, among others. Subsequently, methodologies for crafting efficient, stable, and resilient hydrophobic textiles are elucidated, encompassing conventional techniques as well as novel, inventive concepts. Furthermore, the current state of research and the obstacles faced in the evolution of multifunctional textiles based on superhydrophobic fabrics are examined. In conclusion, this discussion presents incisive insights into the impending direction of advancements in functional textiles.

Keywords: Eco-friendly; Superhydrophobic; Bioinspired; Multifunctional textiles; Natural materials.

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1 Introduction

In recent years, there has been an increasing concern over personal health, which has spurred the development of an increasing number of sensors designed to monitor human physiological and chemical parameters. The conventional mechanical and electronic sensors are often cumbersome and uncomfortable for prolonged wear, prompting researchers to engineer intelligent devices for the human body using innovative materials such as hydrogels,^{1–5} aerogels,^{6–10} and flexible textiles.^{11–15} In addition, electronic skins^{16–20} and human implantable devices^{21–25} are also proposed with prototypes developed. Typically, these devices are expected to be

harmless to both living organisms and the environment. However, the current research primarily concentrates on achieving the desired functionalities, and significant challenges remain in realizing devices that are both environmentally benign and biocompatible.

Natural materials have garnered significant interest due to their exceptional biocompatibility. Plant-derived extracts, including fibers, natural leather, animal fur, and shells, along with their derivatives, have been extensively incorporated into the fabrication of functional textiles.^{26–28} These materials are endowed with a wealth of functional groups and intricate molecular structures, enabling them to form bonds with the plethora of hydroxyl, carboxyl, and other moieties present in textiles. Consequently, a diverse array of techniques for the creation of functional textiles has emerged, encompassing impregnation, spraying,^{29,30} sol-gel processes,³¹ and *in situ* polymerization methods.³² Additionally, the advanced maturity of processes for crafting hydrophobic textiles, coupled with the tangible utility of these functionalities, has predisposed researchers towards the development of multifunctional textiles on hydrophobic substrates. In this vein, numerous eco-friendly, hydrophobic, and multifunctional textiles have been innovatively designed, such as high-performance sensors, alarm systems, and

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energy-harvesting devices constructed from conductive materials like carbon nanotubes (CNT),³³ MXene,^{34,35} graphene,^{36,37} among others,^{38–40} integrated with textile fibers, plant fibers, and other natural materials. The field of green and multifunctional hydrophobic textile design has thus witnessed rapid and progressive advancements.

This manuscript presents an exhaustive examination of eco-friendly techniques for the production of hydrophobic textiles and their functional augmentation. It commences with an elucidation of the wetting state model and the biological orchestration of droplets. The treatise then delves into the exploration of verdant materials utilized in the creation of superhydrophobic fabrics, encompassing natural substances and derivatives obtained from soybeans, plant fibers, seaweed, and crustacean shells, as well as the methodologies employed to engineer highly efficacious and stable hydrophobic textiles. This includes the application of biomimetic principles and sophisticated structural design for bolstering the stability of hydrophobic coatings, coupled with energy-efficient and low energy consumption manufacturing techniques. The third segment elucidates on the versatile textiles spawned from hydrophobic materials, featuring applications such as personal buoyancy aids, proactive perspiration management apparel, and fabrics conducive to monitoring human motor activities. Finally, this paper introduces the obstacles encountered by green hydrophobic textiles and prognosticates the prospective trajectory of their development (Fig. 1).

2 The exploration process of surface wetting mechanism

In the natural world, the phenomenon of bio-manipulation of droplets is ubiquitous. A notable instance of this is the

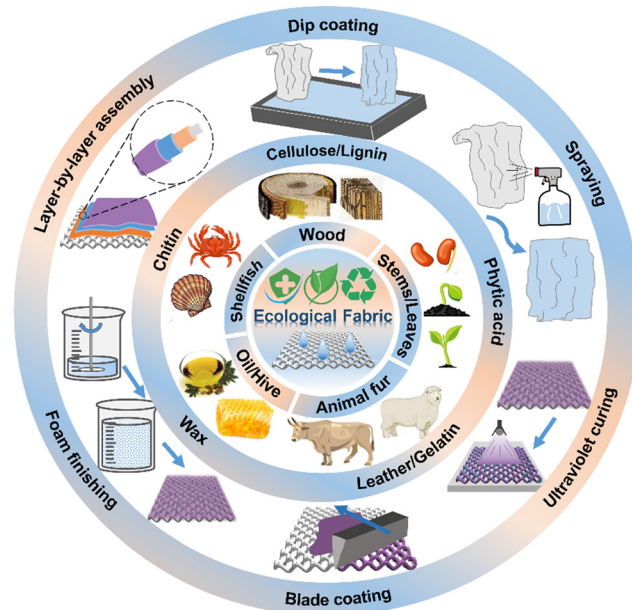


Fig. 1 Natural materials and preparation method for ecological hydrophobic fabrics.

superhydrophobic property exhibited by lotus leaves, which facilitates the unrestricted movement of droplets across their surfaces.^{41,42} This behavior is not unique to lotus leaves but is also observed in other species, such as the feathers of swans and the legs of water striders.⁴³ Researchers have deciphered the enigma of surface wetness and developed techniques for fabricating superhydrophobic surfaces. These surfaces are implemented in various applications requiring water repellency or self-cleaning properties, including the exterior walls of buildings, glass panels, and textile fabrics. The wettability of a surface is commonly measured by the



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preparation of novel materials.

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static water contact angle (WCA) and the contact angle hysteresis (CAH).

As illustrated in Fig. 2f, the Young's model proposes that a surface is considered hydrophilic if the WCA is less than 90° , implying a tendency for the droplet to spread out on the surface, thus forming a significant solid–liquid contact area. On the contrary, when the WCA surpasses 90° , the surface is deemed hydrophobic, indicating a reduction in the attractive forces between the droplet and the surface. The WCA can be calculated using the Young's equation, as shown in eqn (1):

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (1)$$

where γ_{sv} , γ_{sl} , and γ_{lv} represent the interfacial tensions of solid–vapor, solid–liquid, and liquid–vapor, respectively, θ denotes the water contact angle at the interface. It can be deduced from Young's equation that a diminution in the surface energy of a solid leads to an elevation of the static WCA (θ). Young's state is predicated on an ideally smooth and chemically homogeneous solid surface. However, in practice, surfaces invariably exhibit some degree of roughness, which

exerts a significant influence on the water contact angle at the interface. As shown in Fig. 2f Wenzel state, when a surface is roughened, a liquid droplet may entirely imbue the rough cavities. To measure the relationship between surface tension and water contact angle with greater precision, Wenzel introduced the roughness factor “ r ” and proposed the Wenzel equation based on Young's equation:

$$\cos \theta^* = r \cos \theta \quad (2)$$

where r represents the ratio of the actual area to the geometrical surface area, θ^*/θ denotes the external/internal CA. According to the Wenzel equation, when the surface is sufficiently rough, with $r \gg 1$, the Wenzel formula ceases to be applicable. In real scenarios, if the surface is adequately rough, air pockets exist between the droplet and the solid. To further elucidate the wetting relationship between the droplet and the surface, Cassie and Baxter proposed the existence of a composite contact on rough surfaces (Fig. 2f), where contact occurs not only between the solid and the liquid but also between the solid and air. This is described by the Cassie–Baxter equation:



Fig. 2 Surface microstructure of cacti (a) Lotus leaf,⁴² Copyright 2008 Wiley-VCH; (b) rose petal,⁴⁴ Copyright 2008 American Chemical Society; (c) fish scale,⁴⁵ Copyright 2009 Wiley-VCH; (d) peristome surface,⁴⁶ Copyright 2016 Springer Nature; (e) cactus,⁴⁷ Copyright 2012 Springer Nature; (f) droplet surface contact model; (g) underwater Cassie state,⁴⁵ Copyright 2009 Wiley-VCH; (h) the means for characterization of the contact angle hysteresis,⁴⁸ Copyright 2022 Wiley-VCH; (i) droplet transport model on cactus thorns,⁴⁷ Copyright 2012 Springer Nature.



$$\cos \theta^* = \sum f_i \cos \theta_i \quad (3)$$

where f_i denotes the percentage of the total contact area occupied by the contact interface between substance and the droplet, with $\sum f_i = 1$. Within the context of a generally rough surface, trapped air is present under nano-pits, allowing for the presumption of two distinct contact scenarios during droplet interfacing: namely, the percentage of the total area in contact between the solid and the liquid (f_1), or between the air and the liquid (f_2). Because of the WCA = 180° , the Cassie–Baxter equation can thus be reformulated as:

$$\cos \theta^* = f_1(\cos \theta + 1) - 1 \quad (4)$$

The Wenzel and Cassie models represent ideal states of solid–liquid contact. However, the interaction between solid and liquid surfaces may be an intermediate state, not fully conforming to either model, as the droplet does not completely fill the nano-pits indentations of the surface. Grounded in these models and their respective equations, we are justified in believing that the WCA of droplet correlates with the surface energy and the roughness. The Fig. 2a shows the micro-structure of a lotus leaf, revealing the rough, protrusive architecture coupled with hydrophobic wax materials adhered to it. This is pivotal in endowing the lotus leaf surface with its exceptional water-repellency and lends credence to the validity of our inference from a tangential perspective.

Typically, two distinct superhydrophobic states are found on rough surfaces. We previously discussed the non-wettability contact mode exemplified by the Cassie state, wherein water droplets facily roll off the surface. Another mode is the Wenzel state of wetted contact, in which the droplets are secured in place on the surface. As shown in Fig. 2b, demonstrating the “petal effect” with the surface of a rose as an example, the droplets assume a spherical form yet maintain a high adhesion to the petals.⁴⁴ Hence, the crucial notion of contact angle hysteresis is introduced. The advancing angle (θ_{adv}) is higher than the receding angle (θ_{rec}), when droplets roll off on an inclined surface, as depicted in Fig. 2h, and their difference is defined as the contact angle hysteresis (CAH). A lower CAH suggests that droplets can roll off the surface with ease. Fig. 2h illustrates the inclined plane method and the addition/subtraction of liquid method for measuring the CAH.^{48,49} On the petal, one can observe numerous closely-packed micro-papillae, each topped with an abundance of intricate folds, which is pivotal for ensuring the superhydrophobicity of the petal. The waxy covering on the surface of lotus leaves prevents droplets from being trapped in nano-pits, yet the micro-dimensions on the petal surface are larger than those of the lotus, causing droplets to settle into the larger pits and form a Cassie wetting state.

Similarly, when a school of fish swims through water contaminated with oil, they can maintain their cleanliness. The surface of fish scales exhibits superoleophobic properties in water, yet in air, it shows superhydrophilicity and superoleophilicity. As shown in Fig. 2c, regularly arranged

micro-papillae are observed on the fish scales, and further magnification reveals rough structures on these micro-papillae. In water, the surface of the fish scales forms a Cassie state with oil droplets, as shown in Fig. 2g. This state is similar to the superhydrophobicity of a solid surface in an atmospheric environment. At this time, water fills the nanoscale pits between the fish scales and the oil droplets, preventing the oil droplets from penetrating.^{45,50} From the “lotus effect” and the “petal effect” to the special oil-repellent behavior of fish scales, the secrets of surface hydrophobicity have been unveiled. To ensure the isolation between the two substances, a third substance needs to be introduced to isolate and maintain this stable state. Just like the “Leidenfrost Phenomenon”, the steam insulates the droplet from the hot pot, and the droplet exhibits superhydrophobic behavior.⁵¹

Further, the manipulation of droplet behavior is crucial for engineering applications. As shown in Fig. 2d, presenting the inner surface structure of the pitcher plant, with regularly arranged micro-channels on the rocky walls of the pitcher plant’s water sac, allowing unidirectional droplet transport without energy gradients.⁴⁶ The inner wall of the pitcher plant consists of multiple first-order micro-grooves, each made up of about 10 second-order micro-grooves, which are arch-shaped and regularly distributed. It is this unique structure that enables continuous upward transport of the liquid, while downward movement is impeded. In deserts, cacti convey droplets to the root’s absorptive trichomes by utilizing their spines. As shown in Fig. 2e, the microscopic structure of a cactus spine is conical with neatly arranged retroverted barbs.⁴⁷ These droplets are driven in a directed motion by the Laplace pressure gradient produced by the conical structure, together with the surface energy gradient due to the surface roughness. As illustrated in Fig. 2i, the spine of the cactus has a grooved cone shape, with the Laplace pressure difference generated at different radii of the cone being:

$$\Delta P = - \int_{R_1}^{R_2} \frac{2\gamma}{(R + R_0)^2} \sin \alpha dz \quad (5)$$

where R_1 and R_2 represent the radius of spikes at different positions, R_0 is the radius of the water droplet, γ stands for the surface tension of water, α is the half-vertex angle of the spine, and dz is the incremental radius of the spike. It is evident that the Laplace pressure in the area of smaller spike radius is greater than that in the area of larger spike radius, creating a pressure difference that drives the movement of the droplet. In addition, the surface near the tip of the needle is rougher than the tail end surface. According to the Wenzel equation (formula (2)), the rougher tip has better hydrophobicity and higher surface free energy. Therefore, this free energy driving force can be written as follows:

$$F = \int_{l_{tip}}^{l_{base}} \gamma(\cos \theta_A - \cos \theta_R) dl \quad (6)$$

In the formula, θ_A and θ_R represent the advancing and receding WCA at the midpoint of the spine, respectively, and



dl is the integral variable in the direction of length from the area near the tip to the area near the base along the midpoint of the spine. In addition, the parallel grooves produce anisotropic contact angle hysteresis, and such grooves make it easier for droplets to be transported horizontally along the spine, which is similar to the directional transport guided by the grooves of the pitcher plant. Similarly, directional movement of droplets can also be observed on spider silk,⁵² and microscopic observation of the spider silk can also reveal similar conical structures and changes in surface roughness.

From the superhydrophobic phenomena observed on the surfaces of lotus leaves and on petals, to the special movement of droplets exhibited by the spines of cacti and the inner walls of pitcher plants, we have discovered the secrets of droplet behavior in nature. In the textile industry, especially in the development of multifunctional fabrics, hydrophobic behavior is a hot topic of research.

In the past time, the construction of superhydrophobic fabrics often involves the use of fluorine-containing materials. Fluoropolymers have unique physicochemical properties such as excellent hydrophobicity and lipophobicity, good chemical stability and bio-inertness.⁵³ The van der Waals forces between fluoropolymers and other materials are small, so they have a low surface energy when treating the surface of the fabric, which the manufacture of superhydrophobic fabrics becomes easier. However, the fluorine materials significantly impact the ecosystem and pose threats to human health, also limits its use. Of course, it is not necessary to use fluorine materials to improve the hydrophobicity of fabric, where natural materials are also widely developed for superhydrophobic fabrics.

3 The natural material used in hydrophobic fabrics

Although many natural materials are hydrophilic,^{54,55} their excellent biocompatibility and environmental friendliness, have become the subject of heightened interest, in recent years, the researchers have turned their focus to natural materials. In fact, the natural materials can be used in the fabricate of superhydrophobic fabrics.^{56,57} We provide the application cases of different natural materials and their derivatives on hydrophobic fabrics, including the use of natural hydrophobic materials to prepare green hydrophobic fabrics, and there are bold attempts to prepare hydrophobic fabrics using nature hydrophilic materials. Finally introduce other natural materials that provide additional properties on hydrophobic fabrics.

3.1 Natural wax

Wax is one of the hydrophobic substances in nature. Waxy materials come from plants, animals and mineral oils, mainly composed of long chain fatty aliphatic compounds.^{58,59} Hydrophobic fabric can be prepared directly from natural wax. Such as, superhydrophobic coatings were prepared from castor oil spherulites,⁶⁰ carnauba wax,⁶¹ paraffin wax *etc.*⁶² In this

process, wax is directly applied to the fabric. Either made into wax particles or mixed with other nanoparticles and used in the preparation of hydrophobic fabrics.

Other components extracted from wax are used in the preparation of hydrophobic fabrics. Such as, fatty acid (stearic acid,⁶³ lauric acid,⁶⁴ oleic chloride,⁶⁵ *et al.*^{66,67}) are almost always present in the wax of all plants. Waxy materials also contain alkanes, triterpenoids, alcohols,^{68,69} which are effective in reducing the surface free energy of fabrics, and are widely used in hydrophobic treatment, but they are not completely non-toxic and harmless.

3.2 Phytic acid

Phytic acid (PA) is an organic phosphorus compound predominantly found in plant seeds.^{70,71} It has strong acidity and metal chelating capacity and is widely utilized.^{72,73} Zhang *et al.*⁷⁴ employed phytic acid to etch cotton fabrics to create rough surfaces, and combined with the thermosetting resin to prepared superhydrophobic textiles. Phytic acid exhibits a strong negative charge that binds firmly to most cationic charged compounds even at room temperature. It can also form coordination complexes with metal ions. Wang *et al.*⁷⁵ used phytic acid chelated with iron ions to produce PA-Fe particles for the preparation of hydrophobic fabrics. In addition, the excellent flame retardant and conductive properties of phytic acid are also commonly used in the preparation of green fabrics.^{76–78}

3.3 Cellulose

Cellulose is one of the most abundant and widely distributed polysaccharides in nature, and it constitutes the primary component of plant cell walls.^{79,80} Cellulose has excellent mechanical properties and low cost, which makes cellulose based fabrics are widely used. Cellulose is a hydrophilic material,⁸¹ but it is easily hydrophobic modified to prepare green hydrophobic fabrics. For example, direct hydrophobic modification of cellulose fabrics.^{82,83}

Moreover, nanocellulose and cellulose derivatives are also widely used in hydrophobic fabrics modification.^{84,85} The modified hydrophobic nanocellulose particles can not only improve the fabric surface, but also have low surface energy. Such as, Sun *et al.*⁸⁶ mixing the cellulose powder with oleoyl chloride to make hydrophobic cellulose powder, Zeng *et al.*⁸⁷ used cellulose nanocrystals to construct the rough surface of fabric, and combined with cured epoxidized soybean oil to produce superhydrophobic cotton textiles.

3.4 Lignin

Lignin, as a kind of recyclable biological resource with multifunctional properties, is widely used in biomedicine, material chemistry and other fields.^{88,89} Unlike cellulose, lignin possesses a complex chemical structure and is highly resistant to acid, alkali and thermally stable.^{90,91} Similar to cellulose, lignin can also be hydrophobic modified,⁹² prepared nanoparticle,⁹³ its derivatives extracted,⁹⁴ and used



in the preparation of hydrophobic fabrics. In addition, lignin has a polyphenol structure, which allows itself to coordinate with metal ions to form hydrophobic particles. Zhang *et al.*⁹⁵ utilized lignin and its metal ion chelation properties to fabricate fabrics with high hydrophobicity for oil–water separation.

3.5 Chitosan

Chitosan is a natural polysaccharide found in the exoskeletons of animals, bacterial cell walls, and membranes of algae.⁹⁶ Its excellent biodegradability and cell affinity have led to its widespread application in bio-functional materials.^{97,98} Although natural chitosan is hydrophilic, but it can be used in the preparation of hydrophobic fabrics after modification technology. The common method is to improve the surface roughness of hydrophobic fabric by chitosan nanoparticles.⁹⁹ Moreover, chitosan hydrophobic films were also prepared by hydrophobic modification.¹⁰⁰ There are also some reports that demonstrate the potential of chitosan in the preparation of hydrophobic fabrics. Raeisi *et al.*¹⁰¹ prepared a superhydrophobic cotton fabric using chitosan and nano TiO₂, and found that the cotton fabric with added chitosan solution changed from superhydrophilic (WCA = 0°) to hydrophilic (WCA = 62°). Furthermore, the unpredictable surface hydrophobicity created by hydrophilic chitosan and tannic acid,¹⁰² this novel method can replace the traditional fluorine-free or fluorine hydrophobic materials. In this process, chitosan not only improves the surface roughness but also reduces the surface free energy of the fabric.

Moreover, the unique properties of chitosan, including the antimicrobial and flame-retardant qualities, are extensively utilized in the fabrication of functional textiles.^{103,104}

3.6 Other natural materials

Other natural materials are also employed in the preparation of multifunctional textiles. For instance, in methods such as producing waterproof leather from animal hides.¹⁰⁵ Silkworms are fed with silver nanoparticles to enable the secretion of silver silk.¹⁰⁶ Hydrogel composite textile materials synthesized using substances like sodium alginate are applied in the creation of wearable multipurpose textiles.¹⁰⁷ Biodegradable oil–water separation textiles are also produced using natural grasses as the raw materials.¹⁰⁸ Furthermore, materials such as taurine, epoxidized soybean oil, edodes polysaccharides, and sodium lignosulfonate are utilized in the fabrication of flame-retardant textiles (Fig. 3).^{109–111}

4 The design strategies for hydrophobic fabric

To imbue hydrophilic fabrics with the capacity to resist droplets, enhancing their surface characteristics through material modification is essential, yet the methods of preparation play a pivotal role as well. In this section, we first discuss several ways of designing hydrophobic fabrics through some common preparation methods. Secondly, we introduce some energy

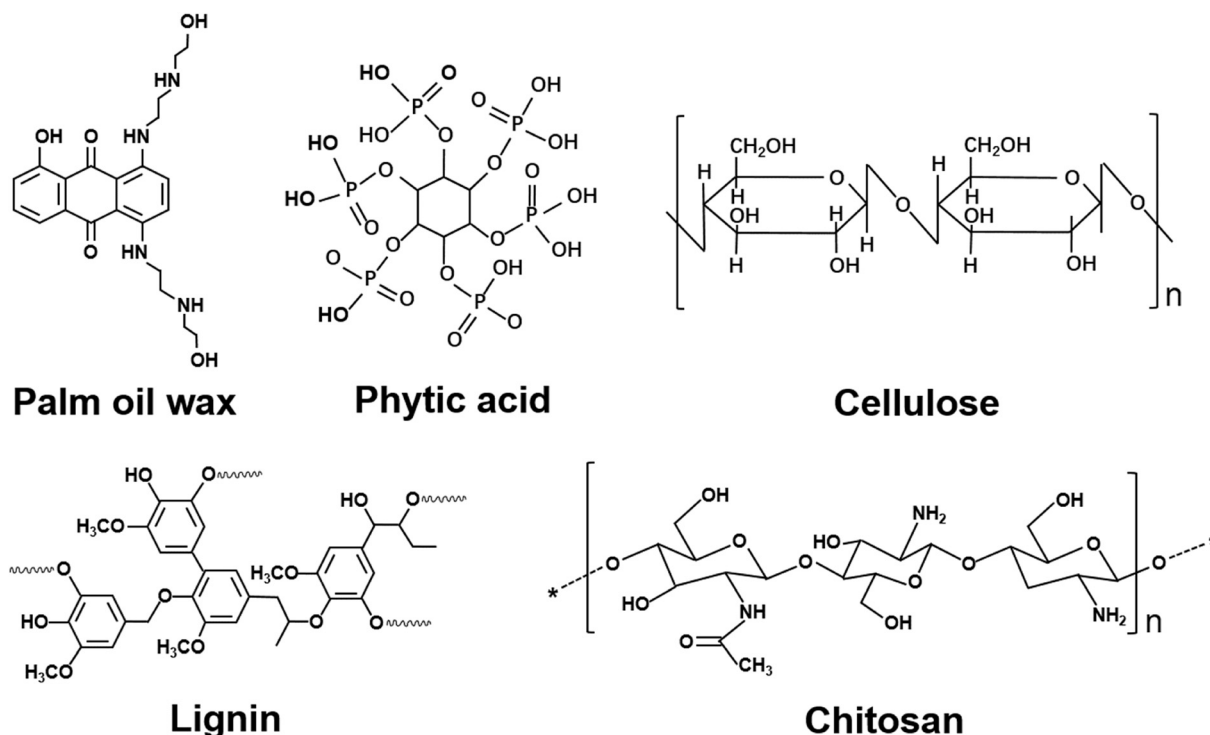


Fig. 3 Natural material structural formula.



saving and fast preparation strategies. Finally, we introduce some inspiring and innovative strategies.

4.1 Recreate the “lotus leaf” surface structure

Most hydrophobic interfaces are designed to mimic the lotus leaf effect, so common manufacture methods of hydrophobic fabrics are based on low energy surface and nano-rough structures.¹¹²

Depending on the hydrophilic and lipophilic properties of natural fabrics, hydrophobic materials can enter the fabric with the solution. Then, the fabric is heat-treated and solvent restored. The fiber is covered with hydrophobic material, and the surface free energy is reduced quickly, so that the fabric can obtain hydrophobic properties. Moreover, the surface of natural fabrics usually has great number of hydroxyl groups, which allows hydrophobic materials to interact with it to form stable chemical bonds. The dipping is one of the most widely used preparation method of hydrophobic fabric in industry.^{113,114} Similarly, spraying, spin coating, and padding also use solvents to transfer hydrophobic materials.

The low surface energy hydrophobic agent is very effective for hydrophobic modification of fabrics, meanwhile, it also important to improving the nano roughness of fabric surface.¹¹⁵ There are three main ways to improve the roughness of fabric:

First, the surface roughness of fabric can be improved by adding nanoparticles. For example, the Fig. 4a proposed a superhydrophobic fabric preparation method based on dopamine polymerization promoted by the Fenton reaction.¹¹⁶ The design promotes dopamine polymerization through the Fenton reaction, and the nanoparticles are firmly wrapped on the fabric, thus forming a surface of nano-rough structure. Moreover, Then the long-term stability between the nanoparticles and fabric was achieved by van der Waals forces.

Secondly, the surface of the fabric can be roughened directly. The Fig. 4b shows a superhydrophobic fabric through a combination of plasma etching and thermal aging.¹¹⁷ The surface of nano-rough structure is effectively formed by plasma etching, and the modification of low surface materials, the formation of hydrophobic fabric. Besides physical etching, the surface roughness of the fabric can be improved by chemical etching (acid-etching)⁷⁴ and biological etching (enzyme-etching).¹²⁰

Thirdly, long-chains are grafted onto the fabric to create a rough surface. As shown in Fig. 4c, long chemical chains are grafted on the superhydrophobic fabric, which are formed by myristate acid and nano-titanium dioxide.¹¹⁸

In addition to the means commonly used for fabric preparation mentioned earlier, nonwovens construct fabrics directly from hydrophobic fibers, such as melt-blowing and

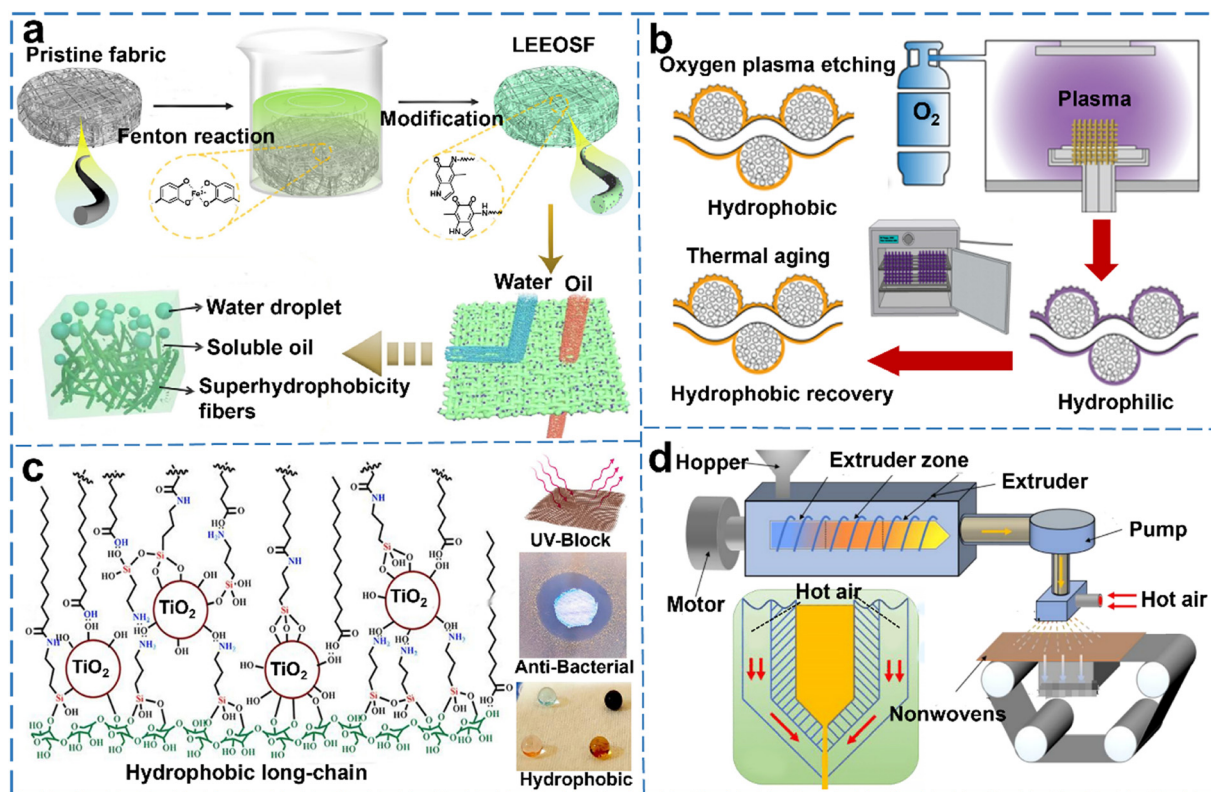


Fig. 4 Preparation of superhydrophobic fabric by (a) Fenton reaction,¹¹⁶ Copyright 2023 Elsevier; (b) oxygen plasma etching and thermal aging,¹¹⁷ Copyright 2020 Elsevier; (c) hydrophobic branches on fabric long chains,¹¹⁸ Copyright 2023 Elsevier; (d) melt-blow method,¹¹⁹ Copyright 2022 MDPI.



electrospinning.¹²¹ As shown in Fig. 4d, the polylactic acid (PLA) and propylene-based elastomer (PBE) polymer are dissolved at high temperature and squeezed into a small spine-jet hole. At the same time, the PLA/PBE polymer are pulled by high pressure and high speed compressed gas, and solidified in the air to form microfibers. This blended nanofiber fabric is hydrophobic.¹¹⁹ Similar to melt-blowing, electrospinning is a process of atomizing polymer fluid to form nanofibers under the action of high voltage electric field.¹²² The fluorine-free fabric by green electrospinning technology has a highly hydrophobic porous structure, the hydrophobic film has ultra-highly water resistance and air permeability.¹²³

4.2 Eco-friendly and efficient treatment methods

Efficient and rapid preparation methods are vital for enhancing production economic benefit of fabrics.^{124,125} Furthermore, traditional preparation methods typically suffer from high water usage and subsequent effluent liquor generation, leading to secondary pollution within the preparation process.¹²⁶ To tackle these issues, Lai *et al.*^{127,128} have introduced a foam finishing

technique for hydrophobic textile treatment. Notably, this method of preparing hydrophobic textiles can reduce the use of aqueous solutions without significantly affecting the breathability and weight of the fabric. As depicted in Fig. 5a, the process involves using surfactants turn an aqueous solution into the foams, replacing water with air as a solvent, thereby decreasing the solution usage. The Fig. 5b demonstrates the impacts of different finishing methods on the liquid pickup, weight gain and breathability of fabrics. The foam finishing method has a lower liquid pickup and weight gain, which means the fabric is quicker drying and energy-efficient. Furthermore, the textile treated with this method are lighter and thinner. Foam finishing method offers advantages, it presented a new idea for the preparation of green hydrophobic textiles.

The foam finishing method constructs a thin and intact film on the textile surface, using a little amount of material, yielding effective protection for the fabric. As illustrated in Fig. 5c, the treated textiles underwent cone calorimetry and thermogravimetric analyses, revealing that the modified fabrics exhibit a stable flame-retardant process. In contrast to traditional methods such as dipping and spraying, which



Fig. 5 (a) Preparation process of foam finishing; (b) liquid carrying rate and air permeability of fabric treated by different means,¹²⁷ Copyright 2021 Elsevier; (c) fabric cone calorimetry and thermogravimetric test,¹²⁸ Copyright 2023 Elsevier.





Fig. 6 Switchable waterborne coatings,¹²⁹ Copyright 2023 American Chemical Society.

thoroughly impregnate the fabric from the outside, the foam finishing approach predominantly deposits materials on the surface of the textile with limited penetration into the fibers.

The sudden change of interface energy will cause huge influence in surface wettability. As shown in Fig. 6, a water-based coating that can be rapidly switched between hydrophobic and hydrophilic.¹²⁹ Taking inspiration from seashells, the team designed an eco-friendly, biodegradable, and naturally derived hydrophobic flame-retardant coating. It is noteworthy that after being processed with a hydrophobic coating, wall surfaces exhibited persistent superhydrophobic and flame resistance, yet upon respraying with a hydrophilic salt solution, the surfaces could be rapidly transformed from hydrophobic to hydrophilic. This design inspiration lays the groundwork for rapidly transforming textiles from hydrophobic to hydrophilic, further enhancing the convenience of practical applications of fabrics.

4.3 Tough hydrophobic coating

The durability of fabric functionality is a critical factor that must be considered for the routine utilization of hydrophobic textiles. As described above, a more stable hydrophobic fabric can be obtained by physical and chemical means, and the mechanical properties of the fiber can also be improved.^{130,131} Besides, the hydrophobic stability of fabric can also be improved by reasonable surface structure design. Here are some innovative design strategies.

Deformable water-resistant surface structure. As shown in Fig. 7a, the superhydrophobic surface is composed of an array of rigid micropillars topped with a soft polydimethylsiloxane (PDMS) matrix.¹³² Under hydraulic pressure, the soft PDMS tips at the top of the structure undergo reversible deformation, in which compression of the PDMS spheres reduces the inter-pillar gaps under applied pressure. This alteration allows the superhydrophobic surface to maintain a stable Cassie state

during compression and impact by water droplets, preventing droplet infiltration. This special structure balance between breathability and hydrophobic of the fabric under various complex wetting conditions.

The rigid structure combined with brittle materials. In general, the hydrophobic modified materials are easily damaged. It is a good strategy to improve the wear resistance of hydrophobic fabrics that using strong structure to protect hydrophobic materials. As depicted in Fig. 7b, a robust armored hydrophobic surface by wrapping waterproof materials in a high-strength array framework.¹³³ When the coated surface is mechanically scratched, the high-strength framework protects the hydrophobic materials from being detached. The mechanical strength of the pyramid structured coating increases with the area of the frame. Although this case does not apply to the preparation of hydrophobic fabrics, it also provides us with a good idea. Similar thinking, the tough fibers can be used to protect hydrophobic materials, it is similarly adding nanomaterials to a body armor.¹³⁵

Soft surfaces resist rigid damage. Xu *et al.*¹³⁴ emulated the soft, wrinkled skin of earthworms and designed a super durable fabric with adaptive deformation, as illustrated in Fig. 7c. The reversible wrinkled surface and the interfacial viscoelastic layer can accommodate mechanical wear and shear forces encountered during washing and friction processes. The mimicking biological behaviors and surface structures has offered significant ideas for the design of hydrophobic surfaces.^{136–139}

In addition to the previously mentioned passive defense mechanism of coatings under external aggression, and the durability of coatings can be enhanced through active self-healing strategies. The self-healing coating of fabric can be divided into internal healing repair and external stimulation repair.^{140–143} The intrinsic repair system refers to the ability of the coating to carry out the repair process independently of



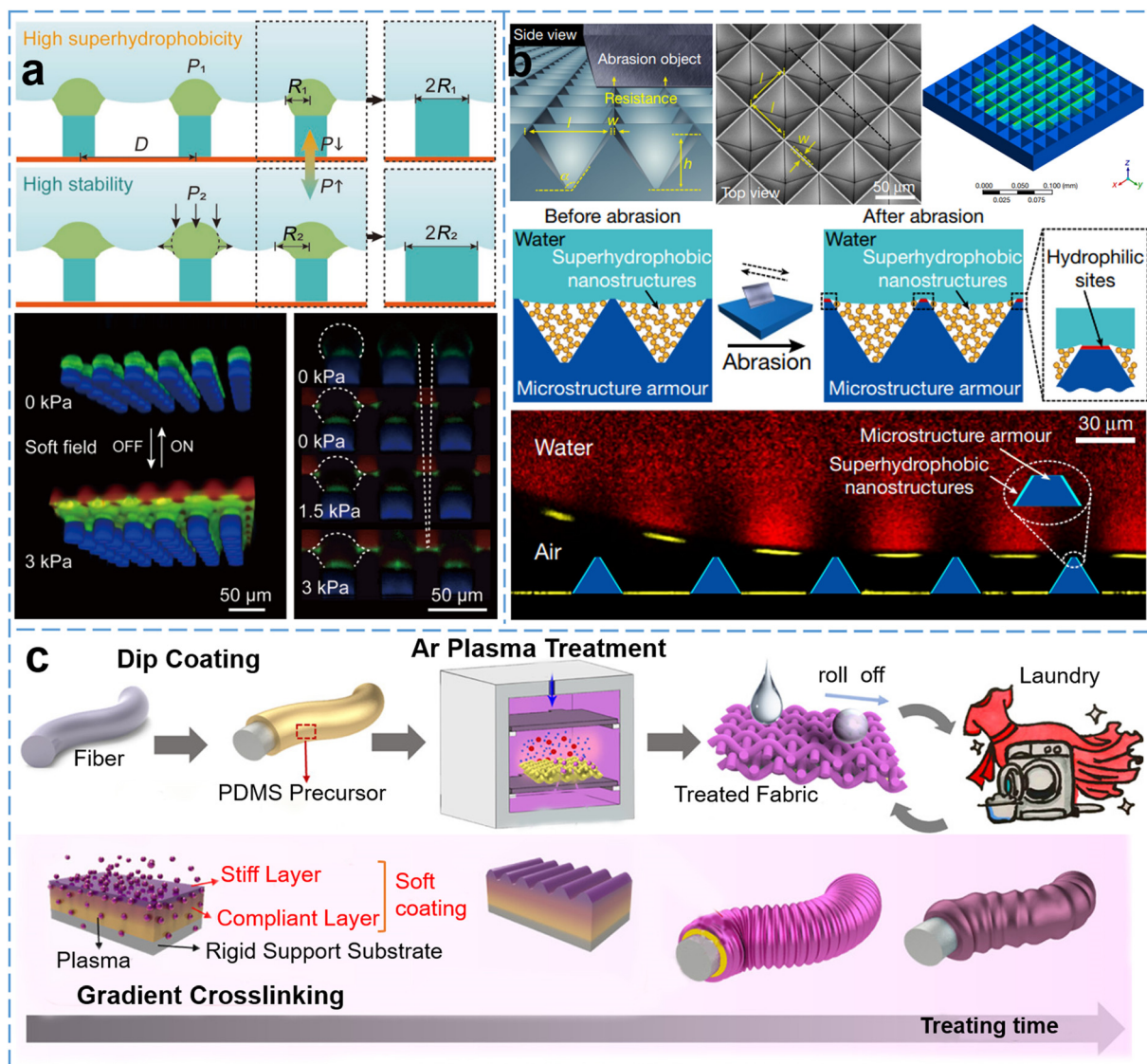


Fig. 7 (a) Design of the LPGSS and its switching effect diagram,¹³² Copyright 2022 Wiley-VCH; (b) design of the microstructure armour,¹³³ Copyright 2020 Springer Nature; (c) SH fabric is prepared by argon plasma treatment and a wrinkled surface is formed on the fiber,¹³⁴ Copyright 2021 American Chemical Society.

external conditions after damage, and thus inspires the design of microcapsules.^{144,145} The external repair coating can be repaired under the action of temperature, pH, humidity, ultraviolet light and other factors.^{146,147} For instance, ultra-thin autonomic healing vitrimer coatings,¹⁴⁸ with the dynamic bonding of the coating material, endows it with self-healing and damage-resistant properties. The Fig. 8 shows the recovery process of the damaged vitreous after reheating.

5 The functional application of hydrophobic fabrics

Superhydrophobic fabrics are extensive application in engineering, with their simplest use being in the creation of waterproof fabric such as storm jackets and tents. The precise manipulation of droplet behavior can be achieved through the

construction of specially wettability fabrics.¹⁴⁹ Additionally, conductive modification hydrophobic fabrics, the conductive polymers can also control the wettability of the fabric and ensure the stability of the conductive stability.^{150,151} The versatility of hydrophobic fabrics is substantial, allowing for integration with numerous functionalities, thereby unlocking greater potential value.^{152,153}

5.1 Functional fabric based on hydrophobic properties

5.1.1 Oil–water separation fabric. The hydrophobic and oleophilic nature of hydrophobic fabrics imparts them with the capability for oil–water separation. The surface energy of oil is lower, allowing it to permeate through the hydrophobic fabric under the gravity and capillary forces, whereas the water unable to infiltrate the superhydrophobic fabric because of its higher



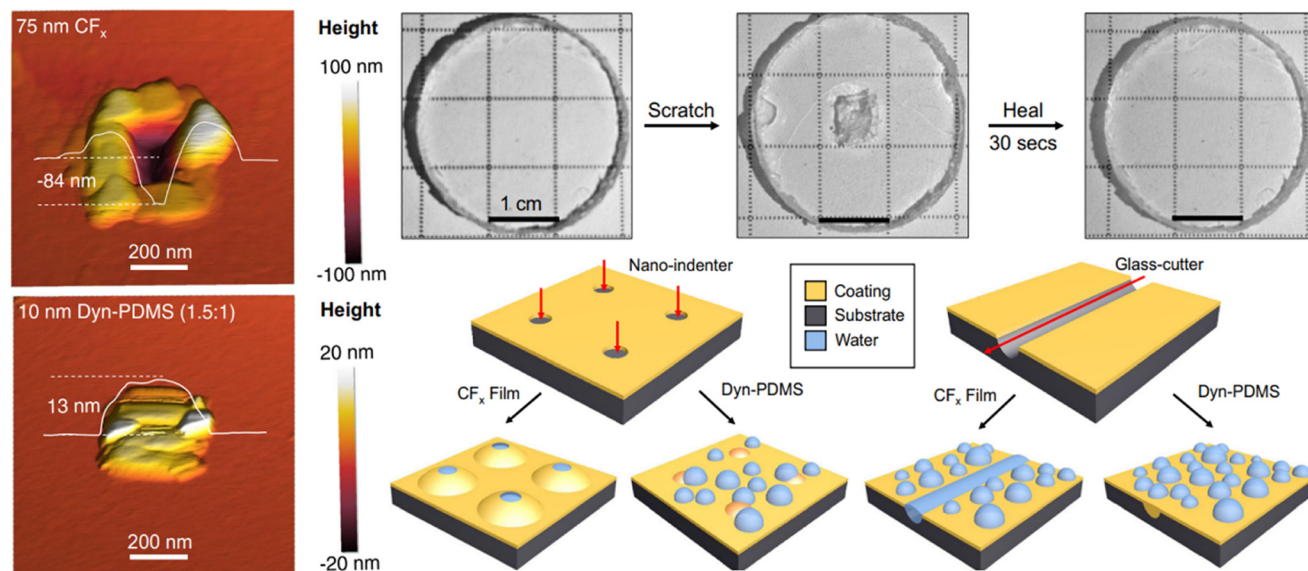


Fig. 8 Self-healing of dynamic crosslinks films,¹⁴⁸ Copyright 2021 Springer Nature.

surface energy.^{154–157} For example, Bai *et al.*¹⁵⁸ synthesized a novel cashew phenol-KH550 benzoxazine (CKBO) by reacting it with 3-aminopropyltriethoxysilane (KH-550) and grafted it onto cotton fabrics. In practical tests, even under harsh conditions, the CKBO-modified cotton fabrics exhibited high separation efficiency for a variety of immiscible oil–water mixtures. Devices designed for this separation based on the fabric substrate are advantageous due to their mechanical robustness and low cost.

5.1.2 High buoyancy fabric. Drawing upon the lotus effect, the rough surface of the lotus leaves traps air when it is in contact with the liquid, thereby preventing the penetration of the droplet and manifesting water repellence in the macroscopic world. The silver mirror phenomenon can be observed when droplets contact the superhydrophobic surface, which is the result of air isolation between liquid and surfaces. Therefore, when the superhydrophobic fabric is immersed in the liquid, a large amount of gas is confined to the surface rough texture, so that the surface has a buoyancy force beyond its own.^{159,160} Zhang *et al.*¹⁶¹ prepared superhydrophobic fabrics using a simple spray process. In the buoyancy tests, the coated filter paper was able to support a weight 39 times of its own. Inspired by this characteristic of hydrophobic fabrics, there are potential applications in drowning prevention or aquatic rescue equipment.^{162,163}

5.1.3 Janus membrane and sweat monitoring. The ease in handling of textile fabrics is a critical aspect in the design process of wearable materials. However, waterproofing and breathability have always represented two diametrically opposed extremes. High-density fabrics can mitigate the penetration of droplets into fibers, yet simultaneously, the breathability of the fabric tends to decrease accordingly.^{164,165} Consequently, the pursuit of fabric that embodies both efficient hydrophobicity and breathability remains a focal point of research.

Fabrics embedded with membranes that exhibit asymmetrical physical and chemical properties, manifested as variations in surface hydrophilicity or charge delineation, are referred to as Janus membranes. Due to their unique asymmetric surface topography, Janus membranes impart specialized fluid transport capabilities,¹⁶⁶ which have drawn considerable interest in the realm of waterproof textile design.^{167,168} Fig. 9a elucidates the diffusion process of water across the surface of Janus fabric.¹²⁷ As water encounters the hydrophobic side, it continues to disperse towards the hydrophilic test direction due to the collective forces of gravity (F_g), capillary force (F_c), and surface tension (F_s), yielding a resultant force is greater than 0 ($(F = F_g + F_c + F_s) > 0$). Conversely, upon contacting the hydrophobic interface, droplets experience radial expansion driven by surface tension and capillary. In scenarios where the aggregate force is overcome by the capillary force, the resultant force is less than 0 ($(F = F_g + F_c - F_s) < 0$), penetration of the droplets through the fabric is inhibited.

For example, Soltani *et al.*¹⁷⁰ have engineered a textile with a Janus membrane structure that facilitates rapid sweat expulsion to ensure human comfort. As depicted in Fig. 9c, the team created a wetting channel on the inner layer of the fabric by wearing two superhydrophobic textiles together. In this configuration, liquid is channeled through a slit into an internal passage, allowing droplets to be transported within the fabric while keeping its exterior dry. This design ensures effective droplet transfer even in highly humid environments. The droplet behavior can also be controlled by external stimulus.¹⁷² The Fig. 9d shows a thermally responsive dynamic Janus fabric.¹⁷¹ When thermosensitive Janus particles adhere to a textile, the surface becomes hydrophobic at temperatures above 32 °C and hydrophilic below this threshold. Therefore, when this composite fabric is worn, the side in contact with skin becomes hydrophobic



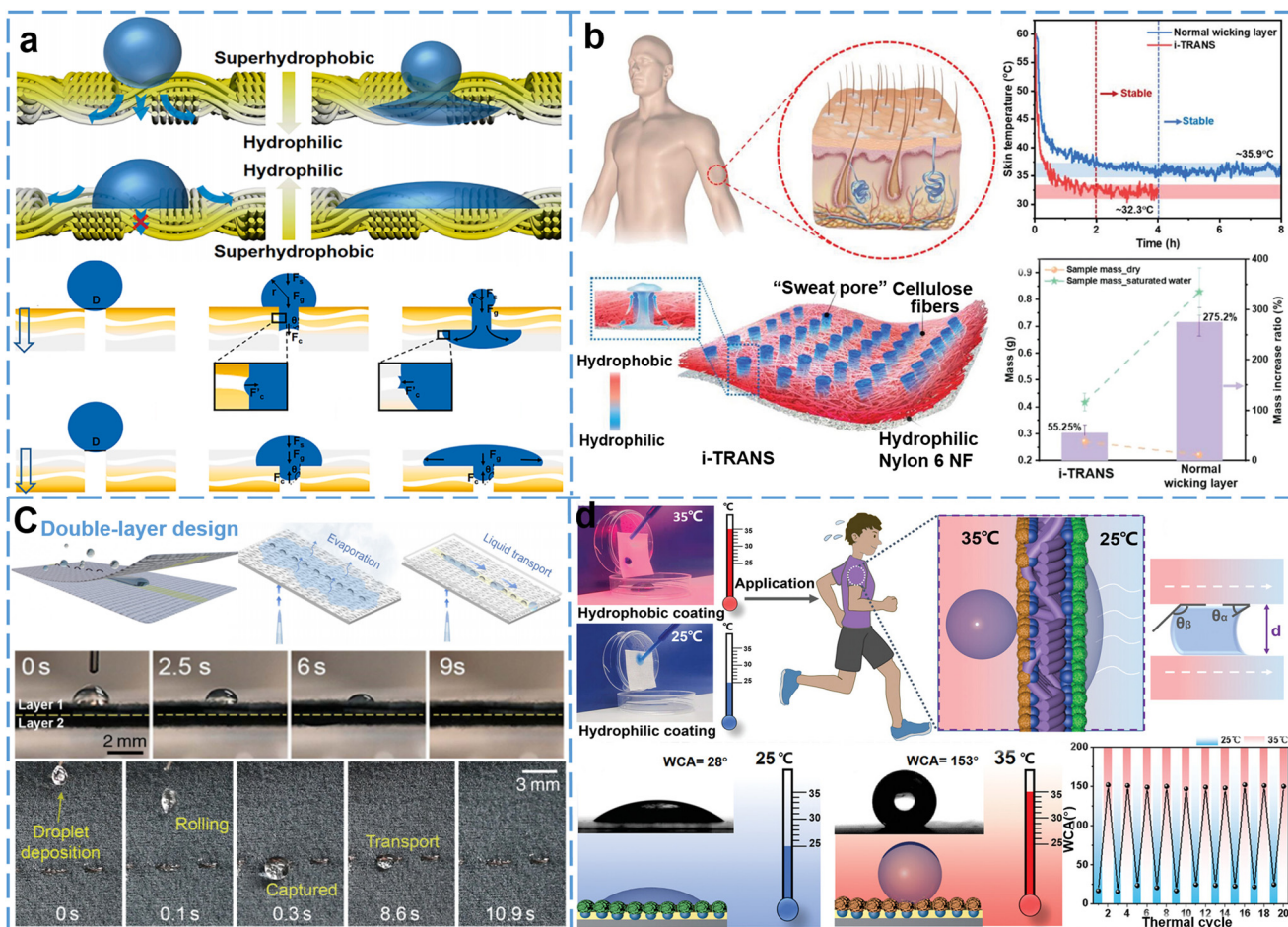


Fig. 9 (a) Janus fabric one-way water transport mechanism,¹²⁷ Copyright 2021 Elsevier; (b) concept illustration of integrated 3D hydrophilicity/hydrophobicity design for artificial sweating skin (i-TRANS),¹⁶⁹ Copyright 2022 Wiley-VCH; (c) schematic of the fabrication of the double-layer fabric assembly,¹⁷⁰ Copyright 2023 The Royal Society of Chemistry; (d) temperature triggered directional water transport fabric,¹⁷¹ Copyright 2023 Wiley-VCH.

due to body heat, whereas the opposite side remains hydrophilic, thereby creating a Janus membrane on two sides of the skin enabling directed sweat transfer. Moreover, there is also a biomimetic skin designed based on Janus membrane characteristics (Fig. 9b), which can effectively facilitate rapid evaporation of human sweat and regulate body temperature.^{169,173–175} It has been demonstrated that the judicious design of fabric structures, combined with the manipulation of physicochemical properties, can engender a differential pressure in droplets, thereby facilitating their autonomous movement.

5.1.4 Fog harvesting devices. By manipulating the gradient of wettability and implementing specialized structural designs, researchers have also developed fog-harvesting and water-collection textiles.^{176–178} Fog harvesting devices, which collect atmospheric water vapor and convert it into liquid fresh water, hold practical significance for addressing freshwater needs in arid regions and for the desalination of seawater. Inspired by the prism-like structures of desert beetle's elytra,¹⁷⁹ Yu *et al.*¹⁸⁰ fabricated a biomimetic, ultralight, superhydrophilic–superhydrophobic (SHL–SHB)

foldable fabric (Fig. 10a). Employing advanced textile manufacturing techniques, yarns with opposing wettability were interlaced, resulting in a vein-like, wedge-shaped structure. SHL yarns are distributed on both sides of the wedge to rapidly capture droplets, while SHB yarns facilitate droplet transport. This wedge-shaped structure, also discernible within the cacti. The curvature gradient along the wedge-shaped track, induces a Laplace pressure difference across the droplet, coupled with fibers of varying wettability, facilitates the directed movement of droplets through capillary action. Special structural is an effective means to drive the droplet, on the other hand, reasonable utilization of the external energy can also achieve on-demand functionality.^{181,182} Fig. 10b depicted a device with high thermal conductivity interfaces and dual asymmetry structures.¹⁸³ The thermal gradient formed on the fabric surface and accelerates the condensation of vapor, while the synergistic action of the wedge-shaped structure and asymmetric wettability gradient provides a potent driving force for the directed transfer of droplets. Experimental results revealed that the maximum water collection rate



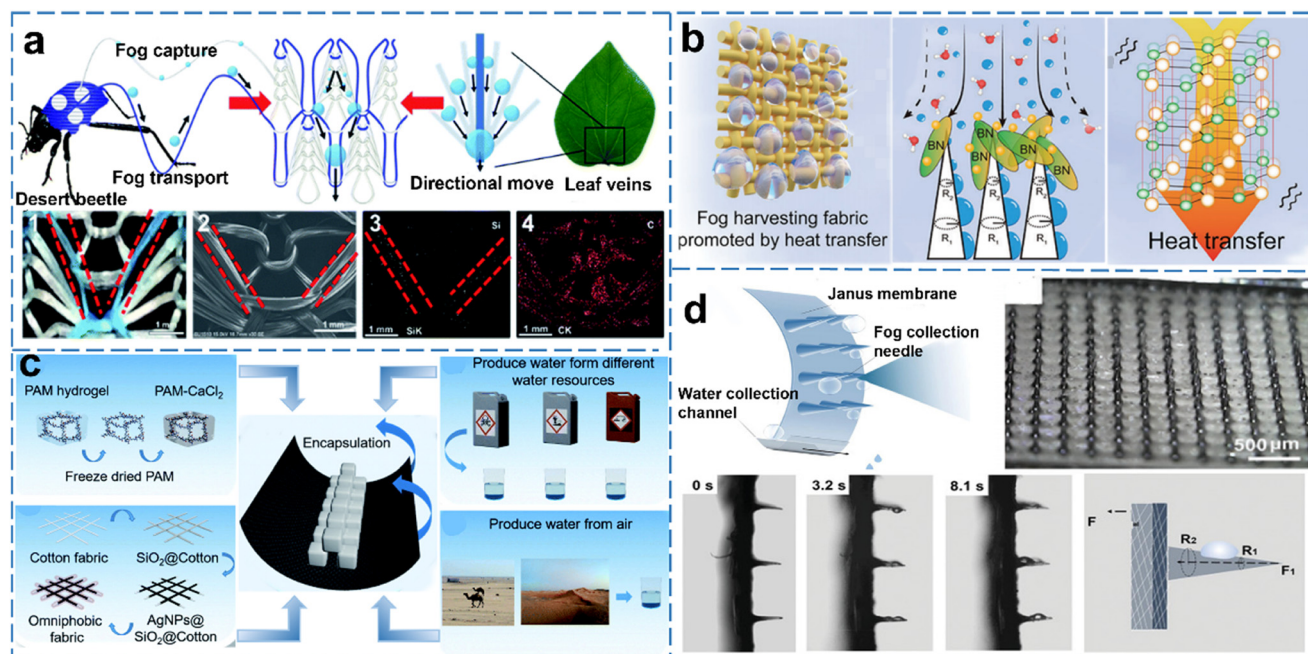


Fig. 10 (a) Double bionic mist collection knitted fabric design,¹⁸⁰ Copyright 2022 The Royal Society of Chemistry; (b) fog collecting process of thermodynamically induced interfacial condensation trap,¹⁸³ Copyright 2023 Wiley-VCH; (c) application of mixed water vapor adsorbent design,¹⁸⁴ Copyright 2021 The Royal Society of Chemistry; (d) observation of the fog collection process and analysis of the droplet transportation mechanism,¹⁸⁵ Copyright 2022 Wiley-VCH.

(WCR) of the fabric-based fog harvester reached 1538.4 mg h cm⁻². Beyond the mentioned fog-harvesting devices, researchers have also developed devices for extracting clean water from wastewater and high-performance devices for seawater evaporation and fog harvesting to collect fresh water (Fig. 10c).¹⁸⁴ Tan *et al.*¹⁸⁵ shows the water collection process using the wedge-shaped structure, promising for application on sailboats to acquire freshwater at sea (Fig. 10d). Fog-harvesting apparatuses based on green fabrics offer favorable biocompatibility and can be widely utilized in natural settings without generating pollution. Additionally, leveraging the unique absorptive properties of the fabric fibers facilitates the control of droplets with greater ease.

5.2 Functional fabric based on hydrophobic and conductive materials

Owing to the effective isolation between hydrophobic fabrics and aqueous solutions, the introduction of electrical conductivity to hydrophobic textiles can yield more favorable outcomes and concurrently facilitate the realization of unique functionalities within the fabric.

5.2.1 Nanogenerator. Nanogenerators have emerged as a research focal point in recent years. The nanogenerator is a nano-scale device, which converts mechanical energy into electrical energy. Nanogenerators mainly include piezoelectric nanogenerators, triboelectric nanogenerators, and thermoelectric nanogenerators, among others.¹⁸⁶ Researchers have utilized the energy generated from human motion to fabricate textile-based nanogenerators, such as the inner and outer rings of fibers made

of different materials can carry different charges,¹⁸⁷ so a potential difference can be created on a single fiber (Fig. 11a left). Charge transfer occurs in external work such as fiber friction or compression, and current is generated under the difference of potential. Moreover, by placing the fibers in series and the fabric layer-by-layer, and the current is increased for use (Fig. 11a right). Furthermore, the repulsive effect of hydrophobic fabrics towards aqueous solutions can maintain the stability of the current produced by nanogenerators and protect the device, marking the development of hydrophobic fabric-based nanogenerators as bearing significant practical application value. Yang *et al.*¹⁸⁸ proposed a novel bio-friendly triboelectric nanogenerator (SF-TENG) based on superhydrophobic conductive antibacterial cellulose. The team employed a unique bioremediation approach to prepare core-shell structures, thereby achieving a superhydrophobic layer on woven fibers. Another example, superhydrophobic cores composite fabric with conductive properties.¹⁸⁹ Integrated nanogenerators boasted advantages such as simple structures and low wear characteristics. Due to the waterproof nature of the fabric surface, the textiles maintained high output performance even under high humidity conditions.¹⁹⁰

Hydrophobic fabrics that integrate nanogenerators and body monitoring have also been extensively studied. Such as, combination of high moisture permeability fiber and nanogenerator,¹⁹² or body motion sensing combined with nano generation.¹⁹³ For example, Hou *et al.*¹⁹⁴ have developed a triboelectric structural material with superhydrophobic and sensing capabilities, which can ensure stable motion monitoring in a high humidity environment. In addition, the



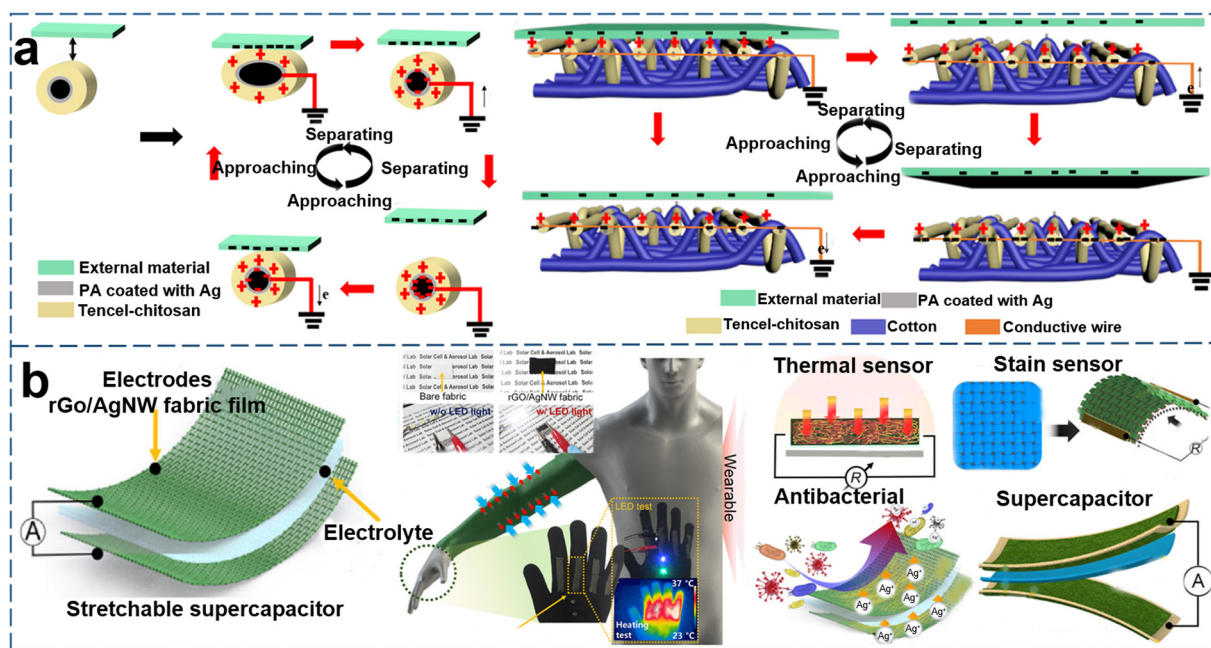


Fig. 11 (a) Structure and working principle of friction nanogenerator,¹⁸⁷ Copyright 2021 American Chemical Society; (b) wearable supercapacitors and human motion sensors,¹⁹¹ Copyright 2021 American Chemical Society.

nanogenerator has wireless signal transmission function, and the motion information of the personnel is transmitted within a distance of ≈ 3 meters. Such cases provide some inspiration for the development of interconnection fabric and intelligent fabrics.

5.2.2 Supercapacitors. Supercapacitors represent a promising energy storage device. They are equipped with advantages such as fast charging rates, stable electrical performances, and high cycle lives, which could meet the application requirements for future wearable devices.¹⁹⁵ Kim *et al.*¹⁹¹ designed a multifunctional fabric that encompasses sensing, heating, and supercapacitor capabilities, along with antibacterial properties (Fig. 11b). Such multifunctional integrated portable electronic textiles hold excellent application prospects in medical monitoring, intelligent active wear, energy storage, and other fields. Additional related examples are also documented.^{196–198}

5.2.3 Human motion sensor. Unlike traditional mechanical devices, fabric sensing devices are thinner and more precise, are thus promising to replace human sensing devices currently available on the market. A variety of human motion sensing devices,¹⁹⁹ leveraging the advantages of the superhydrophobic coating, the sensor can operate under harsh conditions such as moisture, acid, alkali, and salt environments. The fabric is capable of detecting human motion (throat, neck, elbow, wrist, knee, fingers, *etc.*). Sensors for a variety of fields and applications. As shown in Fig. 12a, a fabric-based multifunctional strain sensor with excellent electromechanical performances that can be mounted on joints for activity monitoring, medical rehabilitation assessment, gesture recognition, and other functions.²⁰⁰ Motion monitoring based on waterproof fabrics can offer certain safety guarantees

to individuals working in special environments, like outdoor research teams, divers, and athletes. Body sensors are used in human health monitoring, it has great application potential in the medical field. Wang *et al.*²⁰¹ intercalated a high-sensitivity porous polyethylene terephthalate (PET) sensor between layers of superhydrophobic fabric to design a sensor with high sensitivity and outstanding breathability for sweat analysis. This fabric can be used to assess human life and health conditions such as thermoregulation and skin barrier functions (Fig. 12c). Reports on droplet-based control systems that enable precise measurements are uncommon, underscoring the suitability of conductive fabrics for integration with various functional textiles. Furthermore, the motion sensor applied in life safety field, Lai *et al.*²⁰² developed a silver-rim sensor on superhydrophobic conductive knit polyester fabrics that make use of the characteristics of waterproof textiles. Utilizing the fabric's excellent hydrophobicity (Fig. 12b), conductivity, and mechanical properties, it is feasible to achieve underwater human motion monitoring and drowning alarms, laying a practical foundation for the commercialization of wearable functional fabrics for the human body.^{203,204}

5.2.4 Electromagnetic shielding fabric. With the continuous development of modern electronic communication technologies, there is a widespread need for effective electromagnetic wave shielding materials. These materials serve to protect electronic devices from electromagnetic radiation, safeguarding human health and safety, and they are also of great interest in the defense applications (Fig. 13b).^{205,206} Owing to the excellent flexibility of wearable fabrics and the electromagnetic absorption and shielding properties of fabric conductive materials, the electromagnetic shielding function of conductive fabrics has garnered attention. Conductive materials



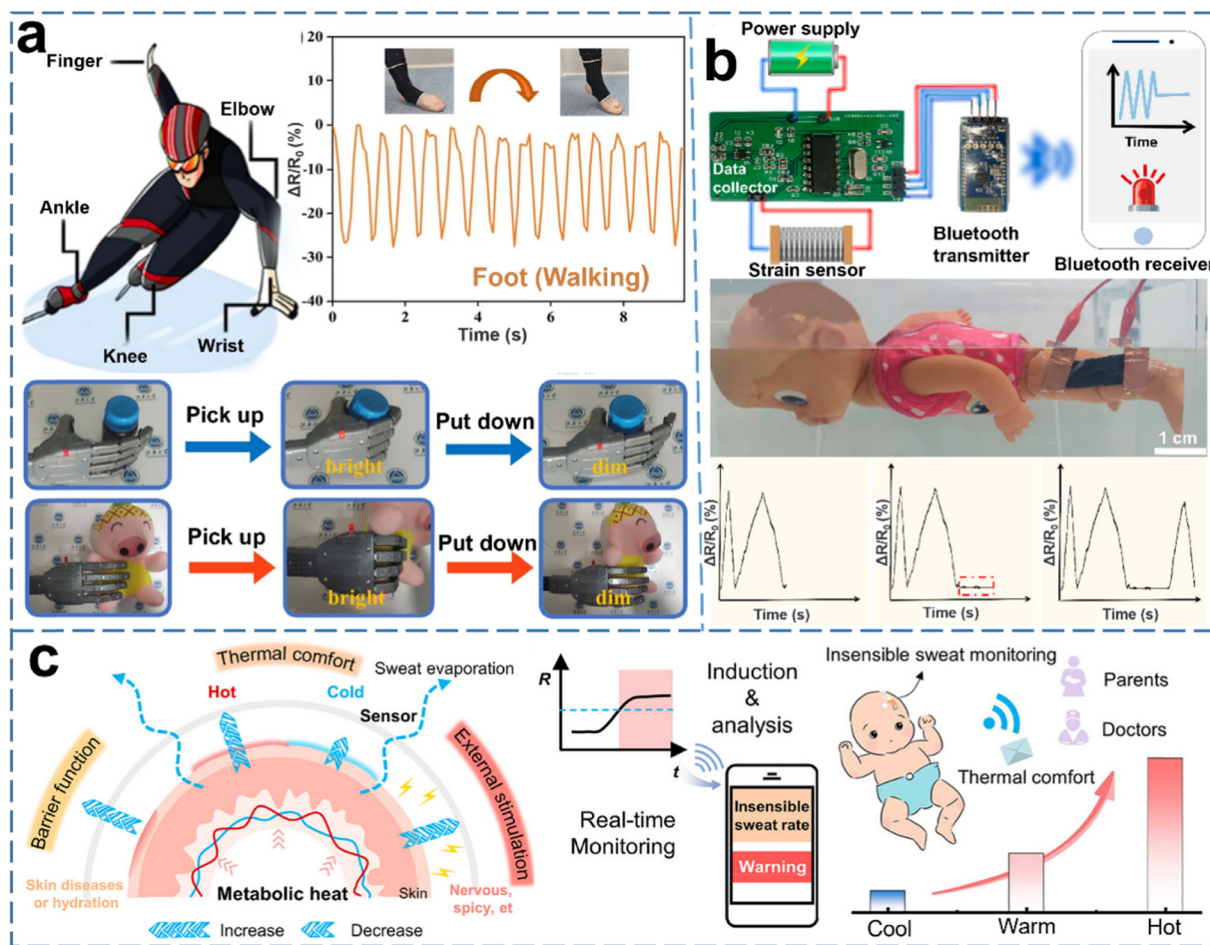


Fig. 12 (a) Multifunctional fabric sensor,²⁰⁰ Copyright 2022 Springer Nature; (b) drowning alarm device based on fabric,²⁰² Copyright 2022 American Chemical Society; (c) application of conductive fabric in medical treatment,²⁰¹ Copyright 2023 American Chemical Society.

are treated on cotton fabrics to form conductive coatings, and the textiles offering outstanding electromagnetic shielding, hydrophobicity, and thermal conductivity.^{207,208}

In the defense domain, textiles with infrared stealth and electromagnetic shielding are widely utilized. Imitated the structure of octopus tentacles,²⁰⁹ achieving adjustable “on-off-on” electromagnetic absorption performance by altering the pore size of the foam skeleton through compressive strain (Fig. 13a). A hybrid strategy by fabricating highly anti-oxidative two-dimensional metal carbides/nitrides (MXene)@gallotannic acid (GA) through Fe^{3+} interactions and covalently grafting the coating onto cotton fabric.²¹¹ Leveraging the antioxidative nature and strong binding properties of GA materials, the fabric maintains good stability, washing resistance, and can withstand various extreme conditions, while achieving excellent conductivity and efficient electromagnetic shielding for infrared camouflage. As shown in Fig. 13c, a multi-function tent featuring electromagnetic shielding and infrared stealth capabilities along with hydrophobic and flame-retardant properties, suitable for tents in harsh conditions.²¹⁰

Additionally, electromagnetic waves often interfere with the monitoring accuracy of the instrument. Han *et al.*²¹² developed a flexible piezoelectric sensor system based on high-performance

electromagnetic shielding signal interference, which can accurately collect and analyze unique physiological sound patterns related to clinical applications, aiding in the diagnosis of heart disease. Liu *et al.*²¹³ developed a highly stretchable, high-permeability liquid metal electronic textile that not only precisely monitors health vitals including respiration, energy generation, surface electromyography (sEMG), and electroencephalogram (EEG) signals, but also maintains commercial electromagnetic shielding requirements under 300% strain (Fig. 14). The preceding introduction outlines a distinct category of fabrics that are enhanced with the capability to shield against electromagnetic interference. This enhancement primarily relies on the creation of interconnected networks facilitated by the high conductivity of surface materials, which in turn serves as a foundation for developing innovative applications within the realm of textile design. However, research aimed at enhancing electromagnetic shielding performance through special designs on ultra-thin fabric coatings remains scarce, despite being a challenging endeavor.

Existing conductive fabrics are primarily functionally independent, capable of realizing only singular or partial functionalities. However, for the realization of highly intelligent fabrics, it is imperative that these textiles integrate multiple



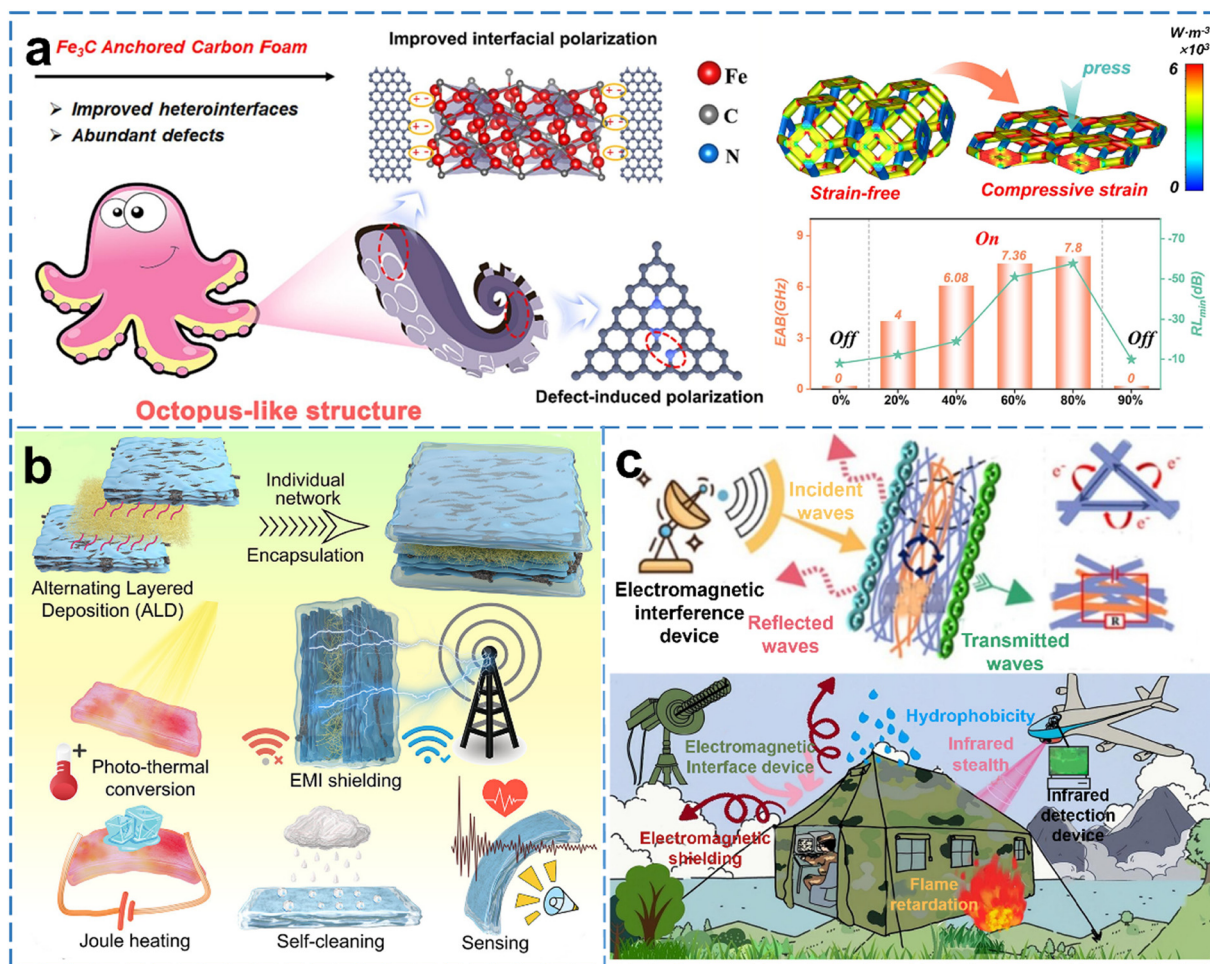


Fig. 13 (a) Bionic octopus structure inspired stress-driven reconfigurable microwave absorption and electromagnetic switching process,²⁰⁹ Copyright 2023 Elsevier; (b) electromagnetic shielding fabric application scenario,²⁰⁵ Copyright 2022 American Chemical Society; (c) electromagnetic shielding fabrics are used in military neighborhoods,²¹⁰ Copyright 2023 Elsevier.



Fig. 14 High precision human physiological signal monitoring wearable chip based on electromagnetic shielding structure,²¹³ Copyright 2023 Elsevier.

functions,^{214–217} such as being powered by nanogenerators, energy storage in supercapacitors, functionality execution within designated zones, and interconnecting communication with external devices. In the future, such intelligent fabrics might supersede our current smart devices, like smartphones and computers.

5.3 Based on hydrophobic fabrics with photocatalytic applications

5.3.1 Self-cleaning, anti-bacterial and ultraviolet shielding fabric. Leveraging the low droplet adhesion and self-cleaning properties of hydrophobic fabrics, researchers have enhanced



these materials by incorporating photocatalytic substances. For instance, by *in situ* deposition of photocatalytic materials on fabric substrates and then hydrophobic finishing, superhydrophobic and photodegradable fabrics have been prepared, endowing the fabric with self-cleaning and antibacterial surface characteristics.²¹⁸ This combination gives the fabric excellent UV resistance, mechanical wear and photocatalytic self-cleaning capabilities.

Photocatalytic materials undergo redox reactions upon exposure to light, in conjunction with the fabric's superhydrophobic behavior, effectively degrading stains adhered to the fabric. Moreover, these materials can also reflect or absorb light waves, harnessing solar energy. Agrawal *et al.*²¹⁹ reported a dual-stage silanization technique for creating superhydrophobic, antibacterial, and UV-protective fabrics. This straightforward fabrication strategy holds significant potential for commercial application in textile materials. There are other reports, a multifunctional fabric prepared with significant hydrophobicity and photothermal effects for oil removal and water evaporation purification.²²⁰ Converting waste textiles into multifunctional photothermal protective materials through carbonization.²²¹

5.3.2 Active heating, deicing and anti-icing. Ice is prevalent in nature and poses detrimental impacts on societal industrial production and daily human life. In general, de-icing strategies can be categorized into passive de-icing based on superhydrophobic surfaces and active de-icing utilizing photothermal and electrothermal materials (Fig. 15a).²²² Zhao *et al.*²²³ introduced a highly efficient fluorine-free superhydrophobic photothermal fabric. Owing to its proficient photothermal conversion property, this fabric could heat the coating to 100 °C at room temperature in 120 s under simulated solar irradiation, demonstrating excellent anti-icing and de-icing performance.

The deicing ability of the superhydrophobic fabric can also be improved by active heating.²²⁴ Fig. 15b shows the electrical conductivity of the fabric and the rate of heating and deicing effect of the fabric under sunlight. Fabrics designed with anti-icing and de-icing functionalities based on these principles can be applied to materials such as storm jackets and outdoor travel tents under extreme ice and snow conditions.

5.3.3 Seawater desalination, solar energy harvesting. Photothermal nanomaterials exhibit exceptional characteristics



Fig. 15 (a) Schematic overview of deicing/anti-icing surfaces,²²² Copyright 2023 Elsevier; (b) conductive fabric active deicing process,²²⁴ Copyright 2022 Elsevier.



such as high photothermal conversion efficiency and broad absorption bandwidth, which can be harnessed for rapid de-icing and seawater desalination. Furthermore, they offer the potential to transform the abundant solar energy into forms of energy required by humans. Xiao *et al.*²²⁵ developed a superhydrophobic fabric composite material for interface-efficient evaporation, as illustrated in Fig. 16a. The fabric comprises a solar energy absorption layer, an insulation layer, and a top-down water transport channel. Utilizing highly hydrophilic PF as a water-absorbing material for efficient moisture wicking and polystyrene foam as an insulating layer, the solar energy absorption layer is constituted of a matrix fabric made from superhydrophobic PDMS and MXene materials. The surface roughness and photothermal properties of the fabric's hydrophobic layer enhance the light absorption efficiency. Moreover, the liquid pumped from below cannot reach the hydrophobic layer, thereby reducing thermal losses from interfacial evaporation, whereas high-concentration brine

returns to the water body driven by a concentration gradient. The insulation layer keeps the upper layer's light and heat separated from the water below, preventing heat transfer to the water body. During the process of evaporation, it is often desirable to attain sufficiently elevated temperatures to expedite the vaporization of liquids. In addition to facilitating rapid temperature increases at the evaporative surface, Xiao *et al.* has also managed to minimize the thermal conduction of heat from the evaporative layer to the body of water.

The following example, employs a clever design that achieves efficient water transport through the construction of a moisture gradient within the fabric, thereby securing highly effective evaporation. Wu *et al.*²²⁹ constructed a novel cotton fabric evaporator with a superhydrophobic-hydrophobic-hydrophilic-superhydrophilic wetting gradient (CEF-WG). The wetting gradient design of CEF-WG efficiently prevents excessive brine from entering the evaporator and effectively reduces thermal losses. Portable solar water purification and



Fig. 16 (a) Schematic diagram of salt deposition and salt tolerance in a brine evaporator,²²⁵ Copyright 2021 Elsevier. (b) Three-dimensional honeycomb fabric solar evaporation seawater desalination schematic diagram,²²⁶ Copyright 2022 Springer Nature; (c) experimental mechanism and performance of smart wearable fluorescent sensing fabric,²²⁷ Copyright 2022 American Chemical Society; (d) schematic diagram of antibacterial mechanism of nanocomposites,²²⁸ Copyright 2023 American Chemical Society.



processing provide an expandable evaporator for solar-thermal applications.

Other researchers have developed a range of solar liquid evaporation devices through special fabric weaving and structural design,^{226,230–233} presenting possibilities for the commercialization of accelerated wastewater treatment, seawater desalination, and drinking water collection (Fig. 16b). Moreover, wearable energy storage fabrics have been designed based on high energy storage capacity.^{234,235}

5.3.4 Luminous quantum dots and fluorescent fabrics. Additionally, there are special fabric materials made utilizing photonic quantum entities. For instance, the surface of the fiber is coated with luminescent nanomaterials, and leveraging the function of photoluminescent nanomaterials, the fabric emits different colors of light under varying frequencies of light radiation (green under ultraviolet irradiation, gray and white under sunlight irradiation, etc.).²³⁶

Moreover, wearable sensing fabrics have been designed based on the integration of fluorescent nanomaterials with antibacterial agents,^{227,228} achieving fluorescence tagging and colony suppression of bacteria (Fig. 16c) and toxic metal ions. Fig. 16d depicts the degradation process of bacterial colonies by antibacterial fluorescent nanomaterials. Such materials

hold significant potential for applications in environmental monitoring and healthcare settings.

5.4 Other types of functional hydrophobic fabrics

5.4.1 Hydrophobic flame-retardant fabric. Under natural conditions, fabrics are susceptible to combustion, posing a fire safety hazard. Therefore, the fabrication of durable flame-retardant fabrics is of significant importance for fire protection.^{237,238} Chattopadhyay *et al.*²³⁹ employed a two-step spray-coating approach to create multifunctional fabrics. The first layer was spray-coated with chitosan and phytic acid to form a flame-retardant coating, while the second layer was coated with PDMS–ZnO to establish a hydrophobic coating. Following modification, the cotton fabric's limiting oxygen index (LOI) increased from 18% to 30%, and its peak heat release rate (PHRR) and total heat release rate (THR) were reduced to 75% and 33%, respectively. The contact angle of the fabric with water was 148°. The combination of green natural materials tannic acid (TA), phytic acid (PA) and polydimethylsiloxane (PDMS) was used to construct an environmentally friendly and efficient hydrophobic flame-retardant coating on cotton fabric using a layer-by-layer self-assembly method (LBL).^{240,241}



Fig. 17 (a) Self-powered fireproof electronic textiles, with temperature monitoring and signal alarm, positioning,²⁴³ Copyright 2022 American Chemical Society; (b) hump-inspired layered flame retardant, heat management fabric,²⁴⁴ Copyright 2023 Wiley-VCH; (c) biomimetic superhydrophobic surfaces to inhibit microbial contamination,²⁴⁵ Copyright 2023 Springer Nature; (d) hydrophobic cotton to promote wound healing,²⁴⁶ Copyright 2021 American Chemical Society.



There are also instances for fire alarm and personal protection applications, such as the design a superhydrophobic, flame-retardant, multifunctional conductive fiber fabric suitable for all-weather wear and high-temperature alarm.²⁴² He *et al.*²⁴³ designed a self-powered fire alarm ultra-lightweight electronic textile based on conductive aerogels (Fig. 17a). Despite the advanced stage of development attained by hydrophobic and flame-retardant fabrics, their presence in the market is surprisingly minimal, a circumstance that might be attributed to their lack of practicality. In the future, researchers might delve into the behaviors of creatures in the natural world, drawing inspiration from biomimicry to craft fabrics with superior functionalities.²⁴⁴ (Fig. 17b, inspired by the structure of camel humps, designed fabrics with personal thermal protection and thermal comfort management). Moreover, steering the development of functional textiles towards real-world applications could foster a paradigm conducive to the creation of more exemplary hydrophobic and flame-retardant materials.

5.4.2 Hydrophobic antibacterial fabric. Similarly, the self-cleaning properties of hydrophobic fabrics can effectively reduce the residual stains on the fabric surface and can also effectively inhibit the proliferation of bacteria and viruses on the fabric surface (Fig. 17c), making fabrics that combine hydrophobic and antibacterial functions a research focus.²⁴⁵ For instance, the fabric is coated with antibacterial materials and encapsulated with hydrophobic materials to achieve hydrophobic, antibacterial and other properties of the fabric.²⁴⁷ Suryaprabha *et al.*²⁴⁸ explored the blood repellency of cotton fabrics and their potential value in the medical field using a coating of chitosan–polyacrylonitrile–polyurethane. Additionally, photocatalytic materials have been introduced to decompose bacterial colonies through redox reactions under light irradiation.^{249–251}

Beyond daily protection, the application of hydrophobic antibacterial fabrics in the healthcare sector is also expanding.²⁵² For example, electronic textiles for human health monitoring and antibacterial properties,²⁵³ and antibacterial cotton fabrics incorporating silver nitrate nanoparticles can effectively accelerate wound healing and sterilization.²⁴⁶ Fig. 17d represents the graphical depiction of wound closure caused by different treatments from day 0 to day 9. Histopathological analysis indicated that the epidermis of the mice treated with cotton fabric impregnated with silver nitroprusside nanoparticles (SNPCFs) was completely healed, with no signs of inflammation or fibrosis. The study suggests that SNPCFs can serve as a new type of agent for wound healing. Textiles hold an irreplaceable position in the realm of healthcare. Medical protective garments and masks crafted from ultra-hydrophobic fabrics can significantly reduce the adherence of bacteria and viruses, thereby diminishing the risk of occupational exposure. Furthermore, functional fabrics used in the production of band-aids and bandages offer assistance in patient recovery, providing a semblance of health assurance. Thus, the design of functional textiles for medical applications is of paramount importance. Table 1 summarizes the preparation process and application of hydrophobic fabrics.

6 Conclusion and outlook

The realization of green sustainability and functionalization of hydrophobic fabrics still requires extensive research and consideration of industrial production. Current fabric design and manufacturing have been moving towards a green and sustainable approach. However, this ‘greenness’ is not all-encompassing, as the manufacturing process is not entirely green or might require a higher cost to make the fabrics healthier.²⁵⁴ Future designs should evolve towards a trend of being green throughout the entire process, cost-effective, and commercialization. With the rapid development of information technology, the Internet of Things, and artificial intelligence, the functionality of various smart textiles is becoming increasingly rich,²⁵⁵ while also gradually being applied in fields such as energy harvesting and resource recovery. Researchers should also focus on the sustainable development of functional fabrics and collaboration across multiple domains (Fig. 18).

6.1 Material selection

As fabrics are intended for everyday use, they should meet basic standards of comfort, non-toxicity to the human body, and durability. In addition, the materials of the fabric should be cost-effective, environmentally friendly, and either naturally degradable or suitable for repeated use. In recent years, natural materials have garnered extensive attention in the preparation of multifunctional textiles due to their excellent biocompatibility and wide availability. Silk, cellulose, phytic acid, and chitosan, among others, have been utilized as foundational materials for multifunctional fabrics to replace other chemical substances. Moreover, the application of cross-linking agents or encapsulating materials to coat textiles can address the issues of wear and oxidation in superhydrophobic fabrics, thereby enhancing the durability of the fabric.

6.2 Process optimization

Today, the textile industry has evolved rapidly and established sophisticated assembly line manufacturing processes. However, high-efficiency production lines and flexible personalized design have traditionally been at odds with each other. In addition, the high efficiency and versatility of production lines are prerequisites for reducing the costs associated with fabric manufacturing and realizing personalized designs of functional fabrics. Therefore, bridging the gap between current industrial production lines and laboratory research conditions to facilitate the translation of functional fabrics from laboratory settings to production applications remains a topic that requires concerted efforts.

6.3 Functional development

Although numerous types of textile products have been invented in the research domain, their functions are mostly basic and discrete. Specifically, various performance textiles exist such as flame retardant, electromagnetic shielding, antibacterial, self-cleaning, *etc.* Likewise, there are textiles designed for applications like nano-generators, biosensors,



Table 1 Preparation and properties of hydrophobic fabrics

Substrate	Modified materials	Fabrication strategy	Wetting property	Function & application	Ref.
Polyester cloth	Hydrogenated castor oil	Dipping	WCA = 156.6°; ^a WSA = 4.8°	Multi-substrate superhydrophobic coating	60
Cotton fabric	Stearic acid; Cu, rGO	Dipping and <i>in situ</i> growth	WCA = 153°	Underwater, multifunctional superhydrophobic sensor	63
Cotton fabric	Lauric acid; γ -Fe ₂ O ₃	Dipping	WCA = 156°	Oil/water separation; flame retardancy	64
Polyester fabrics	Cellulose oleoyl ester nanoparticles	Coating	WCA = 160.9°; ^a SA = 7 ± 1.6°; CAH = 2.5 ± 0.8°	Triboelectric generator; multi-fabric hydrophobic coating	65
Cotton fabric	Phytic acid; stearic acid; epoxidized soybean oil	Phytic acid etching and coating	WCA = 156.3°	Green superhydrophobic cotton fabrics	74
Cellulose nonwoven	Mono-isocyanate compounds	Chemical branches	WCA = 130–135°	Green and breathable hydrophobic fabric	82
Cotton fabric	Lignocellulose	Dipping	WCA = 125.8°; ^a UOCA = 143.6°; ^a UCA = 151.7°	Oil/water separation and seawater desalination	83
Cotton fabric	Oleoyl chloride; cellulose powder	Spray coating	WCA > 150°	Ultraviolet resistant; oil/water separation	86
Cotton fabric	Lignin; Cu, Fe particles	<i>In situ</i> deposition	WCA = 149.9°	Oil/water separation	95
Cotton	Chitosan; tannic acid polymer; PDMS	Dipping	WCA = 153.3°	Ultraviolet resistant; photothermal; self-healing; oil/water separation	102
Polyurethane fabric	Dopamine; Fe nano-particles	Fenton reaction; <i>in situ</i> polymerization	WCA = 161.8°	Structural robustness; oil/water separation	116
Polypropylene fabric	N.A.	Plasma etching and thermal aging	WCA = 180°; SA = 9.8°	Efficient and simple preparation	117
Silk fabrics	Methyltrichlorosilane; papain, alkaline protease	Enzyme-etching; CVD	WCA = 156.7°; SA = 8.5°	Oil/water separation	120
Nonwoven	Waterborne PU; long-chain alkyl polymer	Electrospinning; <i>in situ</i> doping	WCA = 137.1°; ^a RHP = 35.9 kPa	Robust liquid water resistance and water vapor transmission capabilities	121
Nonwoven	Poly(lactic acid); propylene-based elastomer	Melt-blown process	WCA = 134°	Oil/water separation	119
Cotton fabric	SiO ₂ nanoparticles; PDMS	Foam finishing method	WCA = 155.6 ± 1.7°	Energy conservation, efficient and controllable fabric handling	127
Polyester fabric	Pentaerythritol oleate; 3-mercaptopropyltriethoxysilane	Thiol-ene click reaction; spraying	WCA = 171.2 ± 0.3°	Durable hydrophobic coating for multiple substrates; self-healing	146
Nonwoven	TPU; MXene	Electrospinning; dipping	WCA = 145.3°	Pressure-temperature sensing; rechargeable zinc-air battery	163
Cotton	Amino-silica PVDB/PANPAM	Dipping	WCA = 153°	Temperature-triggered dynamic Janus fabrics for directional water transport	171
Cellulose fiber	SiO ₂ nanoparticles; gluconacetobacter xylinum	Bio-fabricated	WCA = 163.5 ± 4°	Fabric-based triboelectric nanogenerators	188
Knitted fabric	Ni; ZnO	Electroplated	WCA = 125°	Antibacterial; supercapacitor; pressure/temperature sensors	196
Polyester fabrics	PDMS; rGO	Dipping	WCA = 156°	Underwater behavior monitoring and drowning alarm	202
Cotton	Polyphosphate; aluminium wire	Dipping	WCA = 130.2°	Electromagnetic shielding, infrared stealth and flame retardance	210
Cotton	MXene; PPy; PDMS	Dipping	WCA = 152°	Joule heating effects and light-to-heat conversion capabilities	224

^a WSA: water shedding angle; SA: sliding angle; UOCA: underwater oil contact angles; UWCA: underoil water contact angles; RHP: robust hydrostatic pressure.

supercapacitors, and so on. The integration of functionalities within textiles is of great importance. For instance, to achieve stable operation of textiles under all-weather conditions and across multiple environments with self-powering capabilities, textiles should fundamentally meet self-powering, energy storage, and functionality requirements. These objectives can be achieved by designing highly conductive circuits on the fabric and implementing zone segmentation, followed by an

encapsulation process to ensure the durability of the integrated functional textiles.

6.4 Interdisciplinary integration

Research in special fabrics should also foster interdisciplinary collaborations, merging with communication technologies, artificial intelligence, and machine learning. First, to realize the





Fig. 18 The future development direction of fabrics.

Internet of Things and create intelligent fabrics capable of cognition, such as smart textiles that monitor human health information and intelligent home systems. Second, their application should span across various fields and settings, including healthcare (prevention, diagnosis, emergency response), exemplified by implanted human monitoring devices and artificial skin; defense applications (camouflage, interference), and space operations (radiation protection, lightweight, temperature control garments). Third, they should contribute to sustainable development through resource and energy harvesting. A widespread collaboration among engineers, scientists, and entrepreneurs is anticipated to facilitate the commercialization of intelligent textiles.

Data availability

All data generated or analyzed during this study are available from the corresponding authors upon request.

Conflicts of interest

The authors declare no conflict of interest.

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