

Recent Progress in Durable and Self-Healing Super-Nonwettable Fabrics

Hua Zhou, Hongxia Wang, Haitao Niu, and Tong Lin*

Considerable interest has been devoted to the development of super-nonwettable (SNW) fabrics owing to their novel functions and enormous potential for applications in diverse fields. The key to practical applications of super-nonwettable fabrics is durability against various damages. Novel strategies have been developed to improve the durability of SNW fabrics. To mimic regeneration ability of natural SNW surfaces, self-healing is introduced. This review summarizes the recent research progress in super-nonwettable fabrics. It summarizes commonly used SNW properties including superhydrophobic–superoleophilic, superhydrophobic–superoleophobic (i.e., superamphiphobic), superoleophobic–superhydrophilic, and underwater superoleophobic fabrics. Strategies to fabricate durable SNW coatings on fabrics are discussed. Special attention is paid toward self-healing SNW fabrics. A perspective on the future development in this field is also provided.

1. Introduction

Super-nonwettability (SNW) is referred to a solid surface with superhydrophobicity or/and superoleophobicity. As a special interfacial property, SNW is widely studied because of the magic liquid-repellent function and enormous potential for applications in daily life and industry. In nature, there are plenty of examples to show superhydrophobicity and underwater superoleophobicity. The most well-known example is lotus leaf, which remains clean despite growing in mud, a real mystery of superhydrophobic property. In 1997, Barthlott and Neinhuis^[1] first elucidated the “lotus effect” mechanism. They attributed the amazing water repellency to a combination of micro- and nanohierarchical surface structures together with a dense layer of hydrophobic epicuticular wax. Later, other natural SNW examples such as *alocasia macrorrhiza* leaves,^[2] rice leaves,^[3] rose petals,^[4] were reported. Apart from the plants, some insects were also found to have superhydrophobic surfaces such as water strider's legs,^[5] butterfly wings,^[4] and cicada.^[6]

Apart from repellent to water, SNWs also include surfaces repellent to oil fluids including organic solvents. Repellency to oil fluids is important because oil fluids are widely involved

in various applications in daily life and industry. For practical applications, SNW surfaces that can repel both water and oil fluids are highly desirable.

For most SNW surfaces, single repellency to water or oil were reported, except for superamphiphobic surfaces. For practical applications, the repellency to both water and oil should be considered. To this end, SNW surfaces should be classified according to their wettability to both water and oil. For example, superhydrophobic surfaces can be classified into oleophilic, oleophobic, superoleophilic, and superoleophobic, whereas a superoleophobic surface can be further classified into hydrophobic, hydrophilic, superhydrophobic, and superhydrophilic. Table 1 summarizes

various types of SNW surfaces according to wettability to both water and oil.

The above-mentioned SNW functions chiefly in the atmosphere environment. These surfaces expose to air during use. SNW surfaces also include surfaces functioning in underwater environment and underwater SNW surfaces were reported recently. A famous example of natural underwater SNW is fish scales, which keep fish's body clean even in oil-polluted water. Such an underwater self-cleaning property stems from a hydrophilic, hierarchically rough surface. It enables water molecules to be trapped in the micro/nanostructured fish scales, facilitating to repel oil fluids.^[7] The subclasses of underwater SNWs are also summarized in Table 1.

Fabrics are flexible, breathable, porous sheet materials having been an integral part of everyday life since prehistoric time. They also function to mitigate surrounding environment change and protect the wearers from mechanical, optical, thermal, and chemical damages. Fabrics with a SNW property but still permeable to air and moisture have attracted tremendous attention in the past decades and will continue to draw much interest in the future owing to the unique performances such as self-cleaning,^[8] antifouling,^[9] anti-icing,^[10] liquid separation,^[11] anticorrosion,^[12] spill-resistance,^[13] drag-reduction,^[14] and personal protection.^[15] However, the main issue hampering the wide applications of SNW fabrics is the poor durability. Most of fabrics lose their SNW after repeated washing, mechanical abrasion, long-hour exposure to sunlight, or chemical contamination. Various methods have been developed to enhance the durability of SNW fabrics, such as covalently bonding the coating to the fiber substrate through active groups,^[16–18] crosslinking the polymer coatings,^[19–21] forming a mechanically robust nanocomposite coating on fiber

Dr. H. Zhou, Dr. H. Wang, Dr. H. Niu, Prof. T. Lin
Institute for Frontier Materials
Deakin University
Geelong, Victoria 3216, Australia
E-mail: tong.lin@deakin.edu.au

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surfaces,^[15,22,23] or introducing a self-healing function.^[24–26] Among these methods, self-healing SNW coating is highly desired for its regenerating ability. Self-healing is an inherent characteristic for living organisms. It enables the damaged or completely lost part to be regenerated.^[27] Lotus leaves have a self-healing capability to maintain their superhydrophobicity. By secreting epicuticular wax to the damaged areas, superhydrophobicity restores.^[28] Recent years, considerable efforts have been made to render artificial SNW coatings with a biomimicking self-healing function, which largely enhances the coating durability.

In previous review papers, the fabrication and applications of superwettability surfaces including superhydrophobic, superoleophobic, superhydrophilic, superoleophilic, under-water oleophobic, and superwettability integration have been reviewed.^[4,27,29–35] Some review articles focus on the fabrication techniques of SNW surfaces, such as plasma,^[36] mussel-inspired superwettable coating,^[37] superhydrophobic coating on cellulose-based materials,^[38] polymeric slippery coatings,^[39] superhydrophobic coatings on magnetic-based surfaces,^[40] the mechanical durability of superhydrophobic materials,^[34] self-healing surfaces with special wetting properties,^[41] and SNW fabric coating strategies and applications.^[35] We have also reported a review article focusing on durable super-liquid-repellent fabrics.^[42] Although the substrates with a single type of superwettability can deal with various practical problems, surfaces with more types of superwettabilities combined together are still required for complex applications.

In this progress report, we mainly discuss the recent progress (since 2008) in the fabrication of SNW fabrics including superhydrophobic–superoleophilic (SHP–SOI), superamphiphobic, superhydrophilic–superoleophobic (SHI–SOP), and under-water superoleophobic (U–SOP). The strategies to improve the coating durability are introduced. Some perspectives on the future research and development in this field are proposed. The fabrication techniques, durability, self-healing test and liquid repellency are discussed in details.

2. Basic Characterization Methods of SNW Surfaces

Surface wettability of solid substances is determined by three parameters, surface free energy, surface roughness, and surrounding media. Therefore, changing any of these factors can modulate the surface wettability. The repellency of liquid on a solid surface is typically evaluated by the apparent contact angle (CA) between the liquid–solid and media–liquid interfaces. When the CA is larger than 150°, the surface shows SNW. Depending on the repelled liquid, SNW surfaces can be classified into air superhydrophobicity against water, superoleophobicity against oils, and superamphiphobicity against both water and oils and in water superoleophobicity against oils.

Apart from contact angle, CA hysteresis (the difference between the advancing CA and the receding CA) is usually used to evaluate the liquid–surface adhesion. Smaller contact angle hysteresis indicates smaller adhesion between liquid and surface. Alternatively, the contact angle hysteresis is characterized by sliding angle (SA), (also known as “roll-off” angle),



Hua Zhou received her PhD degree in materials engineering from Deakin University in 2014. She then joined Deakin University and had worked as Postdoctoral Research Fellow and an Alfred Deakin Postdoctoral Fellow. She is now a Research Fellow in Institute for Frontier Materials, Deakin University. Her research

focuses on functional fibers and smart textiles, including super-liquid repellent, directional liquid transport, and thermal regulating fabrics.



Hongxia Wang received her PhD degree in materials engineering from Deakin University in 2010. After graduation, she joined Deakin University as an Alfred Deakin Postdoctoral Research Fellow, and has worked as ARC Australian Postdoctoral Research Fellow in 2011–2014 and Senior Research Fellow since 2018. Her research

interests include superhydrophobic/superoleophobic coatings, directional fluid transport fabrics, and functional fabrics and nanofibers.

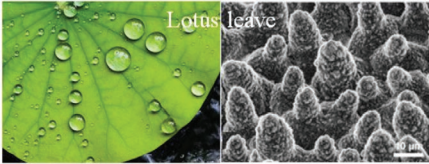
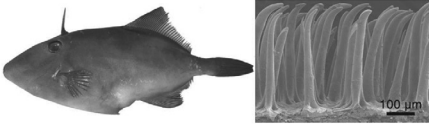


Tong Lin received his PhD degree in physical chemistry in 1998. He is an ARC Future Fellow, Professor and Personal Chair in Fibrous Materials at the Institute for Frontier Materials, Deakin University. His research interest covers functionalized fibrous materials and electrospinning.

which is the critical angle of tilting a horizontal surface to allow rolling off a liquid drop on the surface. CA hysteresis is decided by not only the surface chemistry but also the liquid–solid contact state. In Wenzel state, liquid fully contacts to the surface, usually gives a high CA hysteresis. In Cassie–Baxter state, however, the liquid only intermittently contacts to the solid surface due to the air trapped in the cavities of rough surface, leading to a small CA hysteresis. When a SNW surface has a hysteresis angle less than 10°, it often shows a self-cleaning function.

According to Young’s equation, the apparent CA (θ_c) of a solid surface is calculated as

Table 1. Different type of SNW surfaces and their applications.

State	SNW type		Nature example	Application
In air	Superhydrophobic	Oleophilic/ superoleophilic		Oil–water separation, self-cleaning, anticorrosion, anti-icing, antifogging, antibiofouling, drug delivery, anticorrosion, antifreezing
		Oleophobic/ superoleophobic	None	Antibacteria, antireflection, corrosion resistance, oil capture, oil transportation, self-cleaning, anti-smudge, anti-icing, breathable protective garments, chemical shielding
	Superhydrophilic	Oleophobic/ superoleophobic	None	Antibacteria, antifogging/self-cleaning, oil/water separation, oil capture, self-cleaning, anti-oil-fouling
Under water	Superhydrophilic	Superoleophobic		Antiplaquet, oil droplet transportation, oil/water separation, oil droplet manipulation, device, microfluidic channel, bioadhesion

$$\cos \theta_C = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma} \quad (1)$$

where γ_{SL} is the interfacial tension of the solid–liquid interface, γ_{SV} is the surface tension of the solid. For a liquid with smaller surface tension, the γ_{SL} is also smaller, while the γ_{SV} maintains constant for the same solid surface. As a result, the θ_C tends to be smaller. Liquids having lower surface tension often show smaller CA on the same surface.^[43] In this regard, superoleophobic surfaces often show superhydrophobicity. Shibuichi et al.^[44] first reported a superamphiphobic surface prepared by using an anodically oxidized fractal structured aluminum plate. After modification with fluorinated monoalkyl phosphates, the aluminum surface exhibited super repellency to both water and rapeseed oil. Over recent years, many researchers reported superamphiphobic surfaces. However, some superamphiphobic surfaces are only effective to the liquids with surface tension above 47.3 mN m^{−1} (e.g., ethylene glycol). They became oleophilic to the liquids with lower surface tension. Most of the surfaces can be fully wetted by the oils with surface tension lower than 27.5 mN m^{−1}.

In theory, surface that repel oils also repels water due to the fact that water has a higher surface tension than oils. It is difficult for an oleophobic surface to show hydrophilicity. This is because in Young's equation (Equation (1)), lowering the γ and γ_{SL} would lead to decrease of θ_C . A surface that is repellent to oil fluid is naturally repellent to water as well, and the static contact angle for water (θ_{water}) is generally larger than that of oil fluid (θ_{oil}).^[45–47] In contrast, surfaces that can repel oils but be wettable to water were also reported.^[48–60] Yang et al.^[55] synthesized a complex polymer containing a high surface tension head group and a low surface tension tail group. When it was applied onto a solid surface, the surface showed a low surface tension to repel oil fluids. However, it can be wetted by water, because water can induce the movement of the hydrophilic groups to the top surface. The SHI–SOP surfaces reported so far typically have a poor oleophobicity.

3. Fabrication of SNW Fabrics

The demand on SNW fabrics has been increasing because of their applications in self-cleaning, antifouling, and stain resistance to liquids which offer the wearer excellent protection against toxic, corrosive, or flammable liquids, meanwhile maintain breathability and wear comfort. Similar to SNW surfaces, SNW fabrics can be divided into different types such as SHP–SOI, superhydrophobic–superoleophobic (superamphiphobic), SHI–SOP, and underwater superoleophobic (U–SOP) fabrics. In this section, these major classes of SNW fabrics together with their wetting property and fabrication strategies are introduced in details.

3.1. Superhydrophobic–Superoleophilic Fabrics

To prepare SHP–SOI fabrics through a coating technique, the surface energy of the coating materials should be above that of the oils (15–50 mN m^{−1}), but far lower than that of water (≈72 mN m^{−1}). In addition, surface roughness is another important factor. The inherent microroughness structure of fabrics enhances both SHP and SOI. SHP–SOI fabrics can be used in oil/water separation, oil separation from oil/water emulsion, and underwater oil capture. By adding more functional substances into the coating solution, multifunctional SHI–SOP fabrics can be prepared. The common methods for preparing SHP–SOI fabrics include physical and chemical approaches, such as block copolymer-grafting, block copolymer-grafting, sol–gel, electrospinning, free radical polymerization, nanocomposite, chemical deposition, polymerization reaction, etc. Cotton fabrics are most applied as the coating substrate because cotton contains reactive groups, which can form covalent bonding with the coating substance containing epoxide or silanol groups. Mussel-inspired polydopamine (PDA) has high adhesion to various substrates, even for chemically inert polymers such as polypropylene, which has little reactive groups

Table 2. Preparation and properties of superhydrophobic–superoleophilic fabrics.

Substrate	Materials	Fabrication strategy	Wetting property	Application	Refs.
Nonwoven fabrics	Block copolymer comprising P2VP and (PDMS)	Block copolymer-grafting	WCA $\approx 157^\circ$, and switchable between superoleophobic (OCA $\approx 165^\circ$) and superoleophilic (OCA $\approx 0^\circ$)	Controllable oil/water separation (oil type: gasoline), underwater oil capture (oil type: 1,2-dichloroethane)	[144]
Cotton	PANI and PTES	Vapor phase deposition	WCA $\approx 156^\circ$, OCA $\approx 0^\circ$	Oil/water separation (oil type: hexadecane, chloroform)	[145]
Cotton	TiO ₂ –SiO ₂ @PDMS	Sol–gel	WCA $\approx 157^\circ$, OCA $\approx 0^\circ$	Oil/water separation (oil type: coal oil), colorful pattern printing, drag reduction	[113]
Various substrates (e.g., cotton, wool, textile, glass, plastic, silicon)	Copper acetate monohydrate and hydrazine hydrate	Chemical deposition	WCA $\approx 164^\circ$, OCA $\approx 0^\circ$	Self-cleaning, oil/water separation (oil type: kerosene), antibacterial activity	[62]
Cotton	Fluorinated silyl functionalized Zr	Sol–gel	WCA $\approx 163^\circ$, OCA $\approx 0^\circ$	Oil/water separation (oil type: hexane), self-cleaning	[146]
Cotton	Nano-SiO ₂ @PVDF	Electrospinning	WCA $\approx 157^\circ$, OCA $\approx 0^\circ$	Oil/solvent absorption (oil type: machine oil)	[65]
Cotton	Crosslinkable fluorinated copolymer: (P(MMA-BA-HEMA-FMA-SMA-MAPOSS))	Radical polymerization	WCA $> 150^\circ$, OCA $\approx 0^\circ$	Oil/water separation (oil type: n-hexane, isooctane, chloroform, kerosene, cooking oil)	[147]
Cotton	Silane@Ag/AgBr–TiO ₂ nanocomposite	Nanocomposite	WCA $\approx 149^\circ$, OCA $\approx 0^\circ$	Antibacterial, selective oil absorption (oil type: crude oil, chloroform), UV blocking	[63]
Nonwoven fabric	PS electrospinning nanofibers on fabric	Electrospinning	Superhydrophobic, superoleophilic	Oil absorption, oil/water separation; Oil types: pump oil, colza oil, and diesel	[64]
Cotton	Poly(DMA–octadecyl acrylate)	Free radical polymerization reaction	WCA $> 150^\circ$, OCA $\approx 0^\circ$	Oil/water separation (oil type: soybean vegetable oil)	[148]
Cotton	Hydrophobic SiO ₂ nanoparticles	Sol–gel	WCA $\approx 157^\circ$, OCA $\approx 0^\circ$	Oil/water separation (oil type: diesel)	[149]
Cotton, wool, polyester	PDA/Fe ₃ O ₄ /HTDMS	Chemical deposition	WCA $\approx 156^\circ$, OCA $\approx 0^\circ$	Oil absorption (cooking oil), magnetic property	[61]

*P2VP, poly(2-vinylpyridine); PDMS, polydimethylsiloxane; PANI, polyaniline; PTES, 1H,1H,2H,2H-perfluorooctyltriethoxysilane; PVDF, polyvinylidene fluoride; P(MMA-BA-HEMA-FMA-SMA-MAPOSS), poly(methyl methacrylate-co-butyl acrylate-co-hydroxyethyl methacrylate-co-perfluoroalkylethyl methacrylate-co-stearyl methacrylate-co-methacrylisobutyl polyhedral oligomeric silsesquioxane); DMA, dopamine methacrylamide; PDA, polydopamine; HTDMS, trimethoxysilane.

on the surface. By applying PDA, Fe₃O₄, and hexadecyltrimethoxysilane (HDTMS), Fu et al.^[61] fabricated a durable superhydrophobic coating on fabric surfaces (cotton, polyester, wool), and the use of Fe₃O₄ rendered the fabrics with fast magnetic responsivity. Sasmal et al.^[62] fabricated a multifunctional superhydrophobic coating on various substrates such as cotton, wool, textile, glass, plastic, silicon, through a chemical reduction of copper acetate by hydrazine hydrate at room temperature. The coated surfaces exhibited not only water CA of greater than 164° , but also self-cleaning and oil–water separation abilities. Moreover, the superhydrophobic copper nanoparticles were found to exhibit antibacterial activity. In another work, by employing Ag/AgBr–TiO₂ nanocomposite into the coating solution, a superhydrophobic cotton fabric was prepared, which exhibited multifunctional properties, e.g., antibacterial, UV-blocking, and oil–water separation.^[63] Electrospinning technique was also applied to prepare superhydrophobic coating on fabrics.^[64,65] Through electrospinning process, nanofibrous superhydrophobic porous films were formed on one side of the fabric substrates, hydrophobic polymers such as PVDF, PS were applied for the preparation of superhydrophobic fabrics, and the superhydrophobicity can be further improved by adding nanoparticles into the polymer solution. The coated

Janus fabrics exhibited superhydrophobicity on the electrospinning side and original hydrophilicity on the other side, which can be used for oil/water separation. Most of the SHP–SOI fabric membranes can only separate oil/water mixture, whereas the separation of oil from oil/water emulsion is more difficult. Electrospinning technique can produce nanofibrous membranes on fabric substrate surfaces, thus the prepared fabric membranes can not only separate oil/water mixture, but also separate oil from oil/water emulsions.^[64] Table 2 summarizes various methods used for preparing SHP–SOI fabrics and their applications.

3.2. Superamphiphobic Fabrics

Superamphiphobic fabrics that can repel both water and oil have received a great deal of interest in the past decade because they open the door to a much broader range of applications such as antibacterial, antireflection, corrosion resistance, and self-cleaning. In general, a surface is considered to be superamphiphobic when an organic solvent such as hexadecane (27.5 mN m^{-1}) has CA greater than 150° . To compare with superhydrophobic fabrics, the demands are even strider

for the preparation of superamphiphobic fabrics. Apart from an appropriate surface roughness, fluorinated compounds are important, by modifying straight- or branched-chain molecules with fluorinated groups on fabric surfaces, the intermolecular attraction between the oil molecules and the surfaces become repulsive.

Table 3 summarizes the recently developed superamphiphobic fabrics. Many researchers have reported the preparation of superamphiphobic fabrics using different strategies such as sol-gel, wet-chemical treatment, vapor-phase polymerization, nanocomposite, polymerization, atom transfer radical polymerization, plasma crosslinking, chemical vapor deposition. To create a high surface roughness, most of the methods involved nanoparticles, such as silica nanoparticles (SNPs), Teflon nanoparticles, etc. Fluoro contained materials, such as 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (FAS), fluorinated-decyl polyhedral oligomeric silsesquioxane (FD-POSS), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), fluoro diblock-co-polymer, were widely used to further reduce the surface free energy. By adding functional materials into the coating system, multifunctional superamphiphobic fabrics can be fabricated. Wang et al.^[66] from our group reported an electrically conductive superamphiphobic fabrics through one-step vapor-phase polymerization of polypyrrole (an electric conductive material) in the presence of a FAS directly on fabric.

With the development of superamphiphobic coating technique, recently, durable superamphiphobic fabrics were fabricated that can repel oils with surface tension around 20 mN m⁻¹ or even lower. Li et al.^[67] prepared an abrasion durable superamphiphobic nylon fabric with super-antiwetting property using wet-chemistry method. **Figure 1a** showed the coating procedure that included three steps. The first step was the pretreatment of nylon fabric with polyacrylic acid (PAA) to increase the amount of reactive functional groups on nylon fabrics. The second step involved interfacial reaction based on condensation reactions between water, fabric surface, and trichloromethylsilane (TCMS) to form nanoparticles bonded to the fibers, thus resulting in a robust superhydrophobic nylon fabric. After further treatment using (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (C8-FS), the nylon fabric turned superamphiphobic and can repel oils with very low surface tensions. The coated nylon showed oleophobicity to hexane (18.43 mN m⁻¹), and the CAs were 178°, 152°, and 148° to water (72.8 mN m⁻¹), methanol (22.7 mN m⁻¹), and heptane (20.14 mN m⁻¹), respectively. The roll-off angle was smaller than 10° for oils with surface tension greater than 30 mN m⁻¹. Moreover, the coating was durable against abrasion damages (ASTM D4966, loading pressure 12 kPa). After 15 000 abrasion cycles, the fabric still showed CA of over 150° oils with surface tension greater than 25.35 mN m⁻¹.

3.3. Superhydrophilic–Superoleophobic Fabrics

Common superoleophobic surfaces in normal state are superhydrophobic. In surface physics, superhydrophobic–superoleophilic surfaces are classic to follow the wettability theory because oil fluids have lower surface tension than water. A surface that is repellent to an oil fluid is usually also

water-repellent, and such surfaces often have high water static contact angle (θ_{water}) than the oil static contact angle (θ_{oil}).^[45–47]

There are only limited papers reporting the preparation of SHI–SOP fabrics. For example, Kota et al.^[53] prepared a coating containing cross-linked poly(ethylene glycol) diacrylate (PEGDA) and FD-POSS on solid substrates (e.g., stainless steel mesh and polyester fabric). When an appropriate FD-POSS concentration was applied, a low surface energy of 10.5 mN m⁻¹ was achieved. The coated fabric showed OCA of 152° to rapeseed oil. It required about 20 min for WCA to decrease from its initial value of over 90° to 0°. Molina et al.^[57] prepared a hydrophilic-oleophobic fabric by plasma-assisted polymerization of acrylic acid on cellulosic materials (cotton and filter paper) followed by cationic fluorosurfactant complexation. The WCA of the coated cotton changed from initial 126° to 0° in 60 s, and the hexadecane CA changed from initial 76° to 29° in 80 s. Later, Xu et al.^[59] reported a superamphiphobic polyester fabric that showed SHI–SOP after exposure in ammonia vapor. The fabric was prepared by a dip-coating method to apply a mixture of silica NPs and heptadecafluorononanoic acid-modified TiO₂ sol onto the fabric substrate (**Figure 2a**). Without treatment with ammonia, the fabric showed a CA of above 150° to water, hexadecane, soybean oil, paraffin oil, and diesel. The switch from superamphiphobicity to SHI–SOP was very fast. Within just 3 s of exposure to ammonia, the coated fabric turned the WCA of 0°, whereas the OCA still remained over 150° stably (**Figure 2b,c**). The coated fibrous materials can be used for controllable filtration of an oil–water mixture and selective removal of water from bulk oil.

Apart from ammonia triggered SHI–SOP coating, a UV induced SHI–SOP coating on cotton fabric was reported by Tang et al.^[60] The coating was prepared through layer-by-layer (LbL) assembly of polyelectrolyte multilayers on cotton surface. Perfluorooctanoate was used as counter ions. Without UV irradiation, the coated cotton exhibited superamphiphobicity with $\text{CA}_{\text{water, oil}} > 150^\circ$. After UV treatment, water droplet can penetrate the fabric within seconds, while the OCA remained over 150° to hexadecane.

Although several strategies have been developed for fabrication of unusual water-wettable and oil-repellent coatings, the most of the hydrophilic–oleophobic surfaces show a low oil repellency. Some of the reported SHI–SOP surfaces show either an ageing issue or very short lifetime, i.e., it takes several minutes to change from superhydrophobic to superhydrophilic. SHI–SOP surfaces have important applications in self-cleaning, antifogging, oil/water separation, antibacteria, and other fields.^[55]

3.4. Underwater Superoleophobic (U-SOP) Fabrics

The oil repellent property on the fish scale surface in water was studied. It was found that the U-SOP fish surface stems from the water-phase hierarchical structures, which play a key role in the superoleophilic property in air and superoleophobic property in water. It is well known that in a water/air/solid system, superhydrophobic surfaces stem from the formation of a new composite surfaces. Cassie's theory helps explaining the wetting behavior in the oil/water/solid system. When oil contacted

Table 3. Preparation and properties of superamphiphobic fabrics.

Fabric substrate	Coating materials	Fabrication strategy	Wetting property	Other properties	Refs.
Cotton	Silica NPs, FAS	Sol–gel	WCA $\approx 160^\circ$, WSA $\approx 5^\circ$; OCA $\approx 153^\circ$, OSA $\approx 9^\circ$ for hexadecane	—	[84]
Cotton	Mesoporous silica NPs functionalized with FAS	Sol–gel	WCA $> 150^\circ$; OCA $\approx 155^\circ$ for sunflower oil, $\approx 32 \text{ mN m}^{-1}$	—	[150]
Cotton, wool, polyester	FD-POSS and FAS	Wet-chemical treatment	WCA $\approx 171^\circ$; OCA $> 152^\circ$ for oils with surface tension above 26.5 mN m^{-1}	Self-healing, durable against 200 washing cycles (AATCC Test Method 61-2006), and 8000 abrasion cycles (Martindale Method, ASTM D4966)	[24]
Cotton, wool, polyester	PPy and FAS	Vapor-phase polymerization	WCA $\approx 165^\circ$, WSA $\approx 2^\circ$; OCA $\approx 154^\circ$ for hexadecane	Electroconductive	[66]
Cotton	MWCNTs and PU	Nanocomposite	WCA $\approx 162^\circ$; OCA $\approx 152^\circ$ for hexadecane	Available for various substrates such as paper, PET film	[151]
Cotton	Diblock copolymer PIPSMA- <i>b</i> -PFOEMA	Polymerization	WCA $\approx 164^\circ$; OCA $> 152^\circ$ for diiodomethane, hexadecane, motor oil, cooking oil, pump oil	The coating showed high stability against simulated washing.	[87]
Cotton, wool, polyester	Silica NPs, FD-POSS, and FAS	Sol–gel and wet chemical treatment	WCA $\approx 171^\circ$; OCA $\approx 157^\circ$ and 151° for hexadecane and anhydride ethanol	Self-healing, durable against 200 wash cycles (AATCC 61-2006), 8000 abrasion (ASTM D4966), scratching with a sharp blade, abrasion with sandpaper.	[25]
Polyester	PEDOT, FD-POSS, and FAS	Vapor-phase polymerization	WCA $\approx 169^\circ$; OCA $\approx 156^\circ$ for hexadecane	Electroconductive, self-healing, durable against 500 washing cycles (AATCC 61-2006), 10 000 cycles of abrasion (ASTM D4966)	[26]
Cotton	Silica nanoparticles @P(FOEA- <i>r</i> -IPDMA)	ATRP and sol–gel	WCA $\approx 159^\circ$; OCA $\approx 151^\circ$ for peanut oil	Available for various substrates such as filter paper, glass plates	[152]
Cotton, wool, polyester	Silica NPs, PVDF-HFP, and FAS	Sol–gel and nanocomposite	WCA $\approx 172^\circ$, WSA $\approx 2^\circ$, OCA $> 160^\circ$ for oils with surface tension above 27.5 mN m^{-1}	Self-healing, durable against 600 wash cycles (AATCC 61-2006), 8000 abrasion (ASTM D4966)	[23]
Cotton	Strings of silica NPs, and TEOS, and HDTES	Sol–gel	WCA $\approx 165^\circ$, WSA $\approx 1.5^\circ$; OCAs of 158° and 156° , OSA of 3.5° and 4.0° for olive oil, and hexadecane	Transparent coating, also available for substrates of glass, plastics of PP, PC, PET, durable against heating (up to 400°C), sand abrasion.	[153]
Cotton	DDS–SiO ₂ and fluoropolymer of poly(ST/BA/HEMA/VTPS/PFEA)	Polymerization and nanocomposite	WCA $\approx 163^\circ$; OCA $\approx 156^\circ$ for sunflower oil	Self-cleaning, durable against washing of up to 30 cycles (AATCC 61-1996)	[154]
Cotton	Chitosan, SiO ₂ alcogel NPs, and FAS	Sol–gel, chemical deposition	WCA $\approx 164^\circ$; OCA $\approx 160^\circ$ and 156° for cooking oil and hexadecane	Durable against 10 000 abrasion (Martindale method ASTM D4966) cycles and 30 wash cycles (AATCC Test Method 61-2006), and 98% H ₂ SO ₄	[94]
Cotton, polyester, wool	PVDF-HFP, FAS	Wet-chemistry	WCA $\approx 162^\circ$; OCA $\approx 156^\circ$ and 150° for cooking oil and hexadecane	Durable against 10 000 abrasion (Martindale method ASTM D4966) cycles and 800 wash cycles (AATCC Test Method 61-2006), self-healing ability against chemical damages.	[15]
Cotton, PET	Diblock copolymer (PFOEA- <i>b</i> -P(GMA- <i>r</i> -mOEGMA))	ATRP	WCA $\approx 163^\circ$; OCA $\approx 153^\circ$ for peanut oil and hexadecane	Durable against 80 cycles sandpaper rubbing (lab setup), 50 laundry cycles (lab setup)	[90]
Polyester	PAL nanorods and organosilanes		WCA $\approx 166^\circ$, WSA $\approx 2.2^\circ$; OCA $\approx 153^\circ$, OSA ≈ 17.8 for <i>n</i> -decane	High mechanical, environmental chemical, and thermal durability; Available for various substrates: glass, paper, wood, aluminum plate, PE plate	[118]
PET	Silica NPs, PDMS, and FAS	Sol–gel, nanocomposite	WCA $\approx 157^\circ$; OCA $\approx 157^\circ$ for hexadecane	Durable against acid and alkali (pH 1–14), 2000 abrading (AATCC Test Method 8-2001), 100 commercial laundry cycles (SW-12E, Fang Yuan, China)	[155]
Cotton	Tris-trimethylsilyl copolyacrylate	Polymerization	Hydrophobic and oleophobic	By applying fluorine-free silicone based materials to masonry and fabrics, the coated substrates exhibited hydrophobic-oleophobic property; Anti-stain ability grade 3 (AATCC Test Method 118-2002);	[156]

Table 3. Continued.

Fabric substrate	Coating materials	Fabrication strategy	Wetting property	Other properties	Refs.
Nylon	Polyacrylic acid, silica NPs, and C8-FS	Wet chemistry	WCA $\approx 178^\circ$; OCA $\approx 152^\circ$ and 148° for methanol and heptane	Abrasion durability against 10,000 abrasion cycles (Martindale Method ASTM D4966)	[67]
Cotton, polyester, wool	PFDA, GPTMS, silica NPs	Plasma crosslinking	CA above 150° for oil liquids with surface tension larger than 21.5 mN m^{-1}	Durability against 50 wash cycles (AATCC Test Method 61-2006), 3500 abrasion cycles (Martindale Method ASTM D4966), acid and alkali (pH 1–14)	[81]
PTE, cotton	Diblock copolymer PFOEAm- <i>b</i> -P(GMAx-r-mOEGMAy) <i>n</i>	ATRP	WCA $\approx 162^\circ$; OCA $\approx 153^\circ$ for peanut oil	—	[157]
Polyester	F-SiO ₂ NPs, T-FAS, and FAS	Wet-chemistry and CVD	WCA $\approx 168^\circ$; OCA $\approx 156^\circ$ and 147° for peanut oil and ethanol	Durable against 400 abrasion cycles (AATCC Test Method 8-2001), self-healing against both chemical and physical damages	[158]
Cotton, polyester, wool	PTFE NPs, fluoro-copolymer, FAS	Wet-chemistry	WCA $\approx 172^\circ$; OCA $\approx 152^\circ$ and 151° for paraffin oil and hexadecane	Durable against 200 washing cycles (AATCC Test Method 61-2006), 2000 abrasion cycles (Martindale Method ASTM D4966), acid and alkali (pH 1–14); Self-healing ability against chemical and physical damages	[120]

*FAS, fluorinated alkyl silane; FD-POSS, fluorinated-decyl polyhedral oligomeric silsesquioxane; PPy, polypyrrole; MWCNTs, multiwalled carbon nanotubes; PU, fluorinated polyurethane; PEDOT, poly(3,4-ethylenedioxythiophene); ATRP, atom transfer radical polymerization; NP, nanoparticles; DDS-SiO₂, commercial hydrophobic fumed silica after treated with dimethyldichlorosilane; PET, poly(ethylene terephthalate); C8-FS, (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane; PFDA, 1H,1H,2H,2H-perfluorodecyl acrylate; GPTMS, (3-glycidyloxypropyl) trimethoxysilane; F-SiO₂, fluorinated silica; T-FAS, thiol-ene fluoroalkylsilane; CVD, chemical vapor deposition

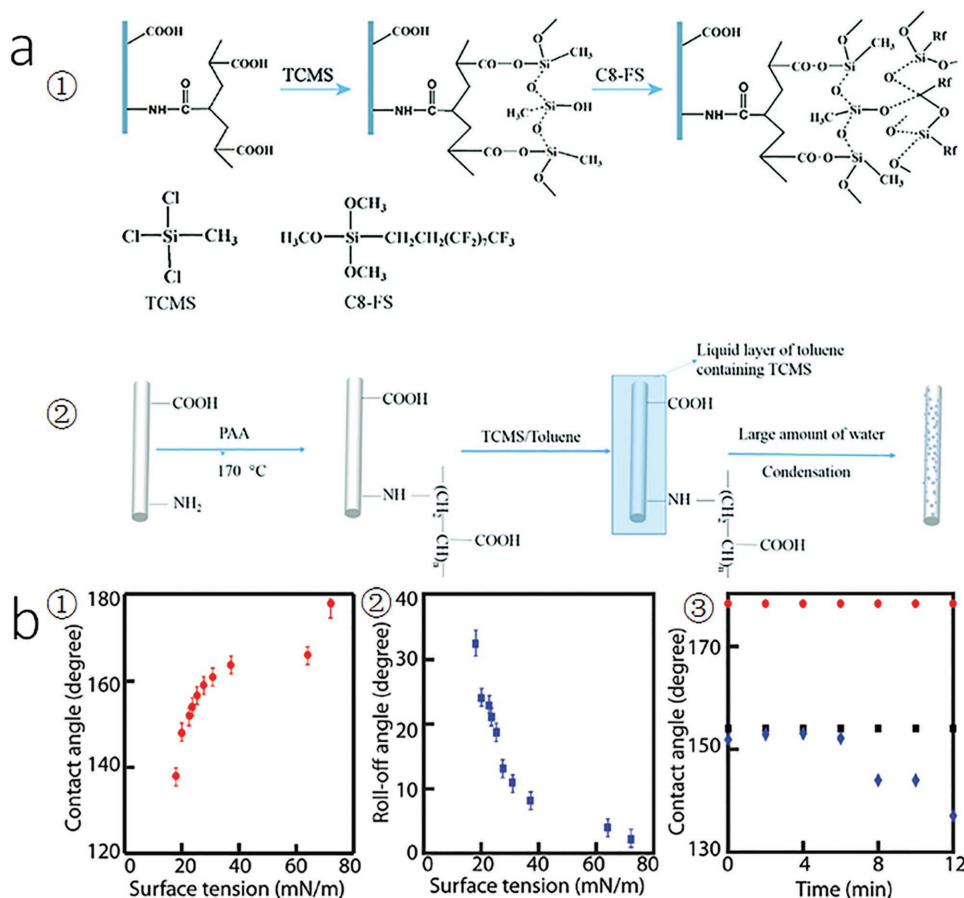


Figure 1. a) The coating procedure for preparing superamphiphobic nylon: ① The scheme of the whole treatment process including PAA, TCMS, and C8-FS treatment. ② The detailed scheme of TCMS treatment step. First a toluene liquid layer with TCMS was formed. Then condensation reaction occurs in the interface area between toluene and water during the washing process. b) The ① contact angle and ② roll-off angle change of the coated nylon with surface tension, ③ the static contact angles of water, dodecane and methanol droplets (10 μL) on the coated nylon. Reproduced with permission.^[67] Copyright 2017, Royal Society of Chemistry.

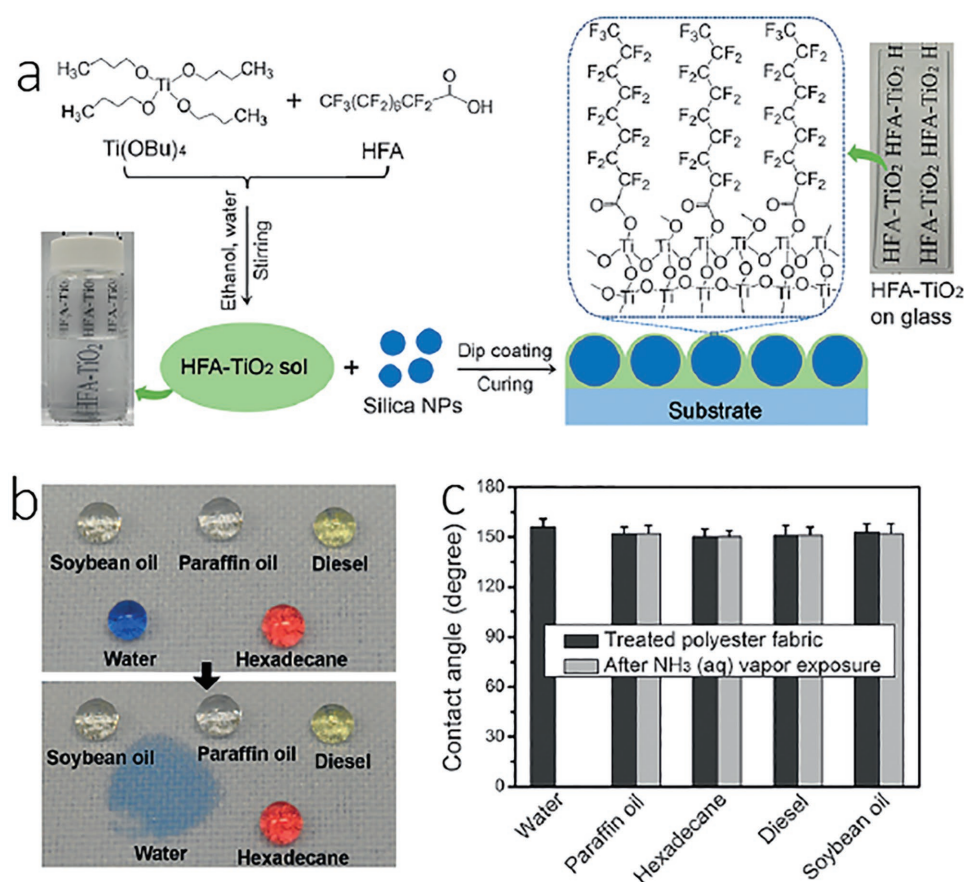


Figure 2. a) Schematic illustration of the preparation procedure for superamphiphobic coating HFA-TiO₂ sol and its coating on glass, b) Photos of liquid droplets on the coated polyester fabric before (top panel) and after (bottom panel) ammonia exposure, c) CAs of the coated fabric to various liquids before and after ammonia exposure. Reproduced with permission.^[59]

with fish scale in water, the water molecules can be trapped in the hierarchical fish scale, forming an oil/water/solid interface, which shows superoleophobic properties. According to this principle, fabricating a U-SOP surface is simple and can be realized through an appropriate surface roughness and the materials showing hydrophilic properties in air.

Inspired by fish scales, underwater SHI-SOP fabrics have been developed in recent years. Zheng et al.^[68] fabricated a U-SOP fabric and studied the oil–water separation properties. Since then, different strategies to fabricate U-SOP fabrics have been developed. Table 4 shows the recent developments in fabrication of U-SOP fabrics. Cotton fabrics were most applied as U-SOP coating substrates due to the nature hydrophilic and underwater oleophobic property, and the abundant reactive groups on the surfaces, which can be bonded with various coating materials. U-SOP coating on other fabric substrates, such as polyester, carbon fabric, wool, were also fabricated by creating a hydrophilic polymeric film or electrospinning polymer nanofiber membranes on the fabric substrates. For example, through electrospinning a hierarchically porous polyvinylidene fluoride (PVDF)–silica composite nano/microbeaded top layer and a PVDF nanofibrous intermediate layer on a nonwoven polyethylene terephthalate (PET) substrate, and further modification with dopamine

solution. Liao et al.^[69] fabricated an electrospun membrane on PET nonwoven substrate. The membrane showed in-air superamphiphilic, underwater superoleophobic, and under-oil superhydrophobic. It can treat various types of oil/water mixtures, from simple layered solutions to emulsions (including surfactant-free or surfactant-stabilized oil-in-water and water-in-oil emulsions). In another work, Fan et al.^[70] prepared superhydrophobic coating on carbon fabrics by forming a zirconium film with mastoids like structure through electrochemical technique. When the superhydrophobic carbon fabric was placed in ammonia vapor, the fabric turned hydrophilic and U-SOP. This switchable fabric can be used for controllable oil/water separation.

Although many U-SOP fabrics have been fabricated, the preparation of durable U-SOP fabrics still remain challenges. Recently, a durable U-SOP wool fabric was fabricated by Feng et al.^[71] Layered polymer nanocoating consisting of a reactive polyisocyanate primer and grafted hydroxyl functional top was synthesized through vapor phase polymerization deposition. The coated wool fabric was durable and can withstand up to 150 washing cycles and 50 abrasion cycles without losing the U-SOP property, and exhibited excellent oil/water separation efficiency of above 99.99% (mixtures of water and different oils with a volumetric ratio of 1:1, oil type: crude oil, diesel,

Table 4. Preparation and properties of U-SOP fabrics.

Fabric substrate	Coating materials	Fabrication methods	Wetting property	Applications	Refs.
Cotton	TiO ₂	Sol-gel	WCA in air $\approx 0^\circ$ OCA in air $\approx 0^\circ$ Underwater OCA $\approx 165^\circ$	Oil (gasoline, edible oil)/water separation UV irradiation recovery	[68]
Cotton	PMAA	SI-ATRP	WCA in air $\approx 0^\circ$ at high pH At high pH, the surface was superhydrophilic and underwater superoleophobic, leading to water uptake in oil. Under ammonia condition, WCA is 150° and OCA is 0°	—	[159]
Nonwoven	PEI crosslinked GO	Sol-gel	WCA in air $\approx 0^\circ$ Underwater OCA $\approx 160^\circ$ for 1,2-dichloroethane	Oil (hexane, octane, isopar G, toluene)/water separation; Antifouling property in oil (Isopar G)/water separation, over 10 cycles	[160]
PET nonwoven	PVDF/silica nanoparticles	Electrospinning	WCA in air $\approx 0^\circ$ OCA in air $\approx 0^\circ$ for petroleum Underwater OCA $\approx 154 \pm 3^\circ$	Underoil WCA $\approx 154 \pm 2^\circ$ Outstanding tensile property and good flexibility Underwater-oil and underoil-water contact angle over 150° over pH range of 1–13 Underwater superoleophobicity with a contact angle of $154 \pm 8^\circ$ and under-oil superhydrophobicity with a contact angle of $157 \pm 2^\circ$ even after being immersed in 90°C water for 30 min Oil (petroleum, dichloromethane)/water separation	[69]
Cotton	Silica NPs and decanoic acid modified TiO ₂	Sol-gel	WCA in air $\approx 150^\circ$ in pH 6.5; Hexadecane droplet absorbed within 66 ms in pH 6.5; DCE absorbed spread out within 1.2 s in pH 6.5 water; WCA in air $\approx 0^\circ$ in pH 12 after 180 s; Underwater OCA $\approx 160^\circ$ for DCE, hexadecane, paraffin oil and soybean oil in pH 12	Oil collection in pH 6.5 Oil/water separation in pH 12 pH-induced wettability transition	[161]
Carbon fabric	Zirconium	Electrodeposition	WCA in air $\approx 0^\circ$ exposed to ammonia Vapor, Underwater OCA $\approx 159^\circ$ for dichloromethane after ammonia treatment	Controllable oil/water separation (paraffin oil/water mixture was tested)	[70]
65% polyester/35% cotton	Copper	Wet-chemistry	WCA in air $\approx 150^\circ$ Underwater OCA $\approx 163^\circ$ and underoil WCA $\approx 155^\circ$ for hexane after $0.4\text{ M H}_2\text{O}_2$ oxidation	Oil/water separation The wettability can be switched by the alternation of weak oxidation and vacuum drying	[162]
Wool	P(IEM-L-HEMA)	Vapor deposition	WCA in air $\approx 0^\circ$ Underwater OCA $\approx 160^\circ$ for crude oil, diesel, vegetable oil, silicone oil, toluene	Oil/water separation Durable against up to 150 cycles of washing, underwater OCA above 155° and separation efficiency above 99.99%	[71]
Polyester	Thiol-ene/silica	Vapor-liquid reaction	Water droplet spread out within 0.36 s OCA $> 150^\circ$ for hexane, kerosene, chloroform, 1,2-dichloroethane, soybean oil, petroleum ether	Oil/water separation. Separation efficiency for chloroform/water mixture and 1,2-dichloroethane/water mixture was 99.5%. hexane/water, kerosene/water, soybean oil/water and petroleum ether/water separation efficiency were all above 96%.	[163]
Cotton	Hydrophobic nickel stearate particles	Wet-chemistry	WCA in air $\approx 158.6^\circ$, 1,2-dichloroethane (DCE) rapidly spread out on the surface DCE droplet was completely absorbed by the fabric; underwater OCA $\approx 154.6^\circ$ for DCE in water after ammonia vapor treatment	Oil-removing or water-removing in oil (toluene)/water separation with separation efficiency over 97% Separate water-in-oil and oil-in-water emulsion	[164]
Cotton	Corn straw powder, polyurethane	Spray coating	OCA $\approx 0^\circ$ for chloroform in air WCA $\approx 0^\circ$ in air Underwater OCA $\approx 155^\circ$ for chloroform Under <i>n</i> -hexane WCA $\approx 152^\circ$	Light oil/water/heavy oil separation (separation efficiency $> 97\%$)	[165]
Cotton	Immersing in NaClO ₂ solution	Wet-chemistry	WCA $\approx 0^\circ$ in air Underwater OCA $\approx 156^\circ$ for chloroform	Oil/water separation (separation efficiency $> 95.7\%$) for <i>n</i> -hexane, toluene, gasoline, kerosene, diesel	[166]
Cellulose	Konjac glucamannan	Wet-chemistry	WCA $\approx 0^\circ$ in air Underwater OCA $\approx 161.1 \pm 0.6^\circ$ for dichloromethane	Oil-water separation efficiency ($> 99\%$) for dodecane against acidic and alkaline environments. Removing water-soluble pollutants such as polyaromatic MB	[167]

*PMAA, poly(methacrylic acid); SI-ATRP, surface initiated atom transfer radical polymerization; PEI, polyethyleneimine; GO, graphene oxide; PET, polyethylene terephthalate; TiO₂, titanium oxide; DCE, 1,2-dichloroethane; P(IEM-L-HEMA), poly-(hydroxyethyl methacrylate-co-isocyanatoethyl methacrylate)

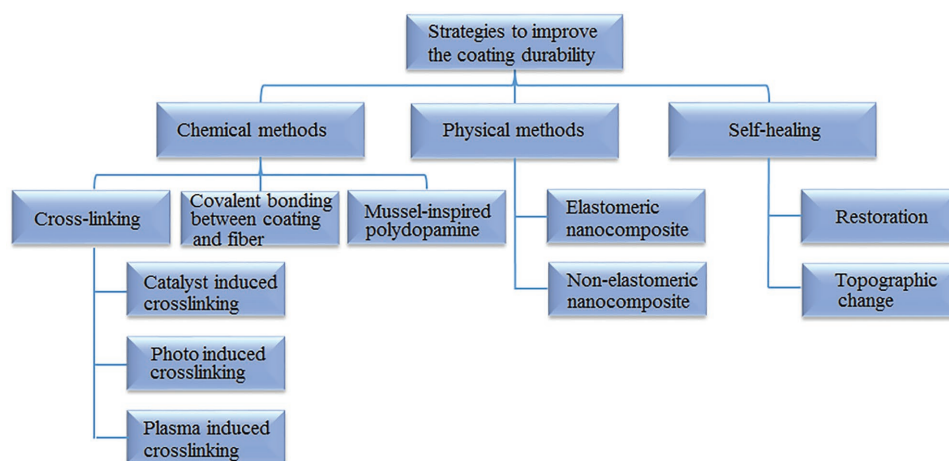


Figure 3. The reported strategies to improve the SNW coating durability on fabric substrates.

vegetable oil, silicon oil, toluene). The fabric can maintain the separation efficiency of 99.99% even after 100 separation cycles.

4. Durability Test Method for SNW Fabrics

Washing and abrasion are very common processes for fabrics and they are the main cause of degradation during practical use of fabrics. So far, there are still no standard test methods specific for evaluation of SNW fabrics. Various washing procedures were applied to evaluate the washing and abrasion durability. For the evaluation of washing durability, the commonly used method is AATCC 61 Standard, which is mainly used for evaluation of color fastness of fabrics to laundering. Apart from the reference of standard washing procedure, lab-built washing methods were also applied, however, these methods varied in different washing parameters, such as detergent type and concentration, washing temperature, and time, etc. For the evaluation of abrasion, Martindale Abrasion Method (ASTM D4966) and AATCC Standard Method are applied mostly. Apart from these standard methods, many other abrasion procedures, such as sandpaper abrasion, blade scratching, tape adhesion, finger press, and hand twisting were also employed. All these mechanical tests are designed by each research groups, and many influential parameters that vary from lab to lab may result in different abrasion durability.

Apart from washing and abrasion evaluation of SNW fabrics, many other resistance of the fabrics, such as acid/base stability, solvent stability, UV stability, high temperature, and humidity stability were also evaluated by many research groups, the testing methods are vary from each to other. Thus it is difficult to compare the SNW techniques developed by different research groups since they employed various evaluation methods.

5. Improvement of SNW Durability on Fabrics

In general, practical use of SNW fabrics requires the functional surface withstanding repeated washing, physical abrasion, or UV irradiation. Depending on the application fields, the durability against special damages, such as corrosion in acid,

base, salt, organic or inorganic environment, high temperature, high humidity, may also be required.

How to prepare durable SNW fabrics without apparently altering the fabric handle, breathability and aesthetic appearance has attracted great attention of scientists. Basic strategies to improving the overall durability of SNW fabrics, especially for those prepared through a surface coating technique, can be divided into two routes: one is to enhance the coating adhesion on fibers, and the other is to introduce a bioinspired self-healing ability into the coating. **Figure 3** summarizes the methods reported for improvement of SNW durability, which can be characterized into chemical, physical and self-healing catalogues. In this section, recent development in improving SNW coating adhesion on fabrics is described.

5.1. Chemical Methods

5.1.1. Cross-Linking with Coating Layer

Cross-linking the coating layer was developed as an effective technique to improve the durability of the coating. Many research studies have been reported about using a crosslinking technique to improve the durability of SNW coating on fabrics.^[18–22,72–79] This method can be used for not only polymer coating but also polymeric nanocomposite coating. Crosslinking can be achieved by addition of crosslinking agent, UV irradiation, plasma treatment, or heating. After crosslinking, the coating durability can be improved.

Catalyst Induced Crosslinking: Su et al.^[79] fabricated a durable superhydrophobic polyester fabric using tetraethyl orthosilicate (TEOS) and dihydroxyl-terminated PDMS as reactants and HCl as catalyst. **Figure 4** shows the procedure for fabricating superhydrophobic PDMS@silica coating on the fabric surface. Here, silica generated from the hydrolysis condensation of TEOS gradually aggregated to form microscale roughness under the driving force of the polarity difference between silica and (PDMS-OH), and the cross-linking reaction of Si-OH groups between aggregated silica and PDMS-OH. The coated fabric showed a water CA of 160°, and the coating was durable against

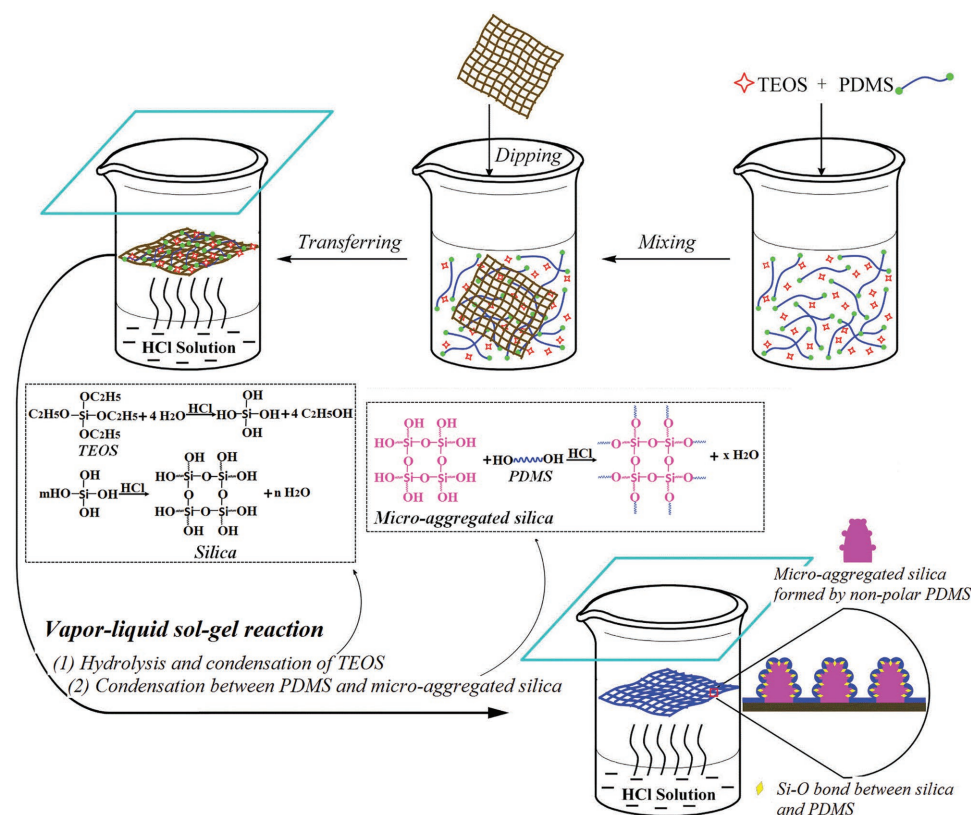


Figure 4. Schematic illustration for fabricating superhydrophobic fabric using PDMS@silica coating. Reproduced with permission.^[79] Copyright 2017, American Chemical Society.

many treatments, such as long-hour ultrasonic treatment, 96 cycles of washing test (AATCC Test Method 61-2006-2A), and 600 abrasion cycles (Lab setup: 280 mesh sandpaper with load pressure of 2.5 kPa, pulling speed of 4 cm s⁻¹, dragging distance of 20 cm for one cycle).

Photo Induced Crosslinking: Zhao et al.^[21] prepared a durable superhydrophobic coating on cotton fabrics through alternatively LbL self-assembly of azido-terminated silica nanoparticles and poly(allylamine hydrochloride) onto cotton surface. UV irradiation was then employed to build a covalent cross-linking network among nanoparticles, polyelectrolyte chains, and cotton substrate. The coated cotton fabric exhibited very good durability against acid/base attacks and organic solvents (ethanol, acetone, ethyl acetate, toluene, and dimethyl formamide), and the fabric can also maintain the superhydrophobicity after 50 standard laundering cycles (AATCC Test Method 61-2006). In another work, Qiang et al.^[76] reported a durable superhydrophobic fabric coating prepared via fast UV-curing method without heating. Cotton fabric was firstly dip-coated by a homogeneous solution of vinyl-terminated polydimethylsiloxane (V-PDMS), tri-functionality vinyl perfluoro decanol (TV-PFOD), and octavinyl-POSS (OV-POSS), and then was cured by UV irradiation for just 1 min to obtain a durable superhydrophobic fabric (Figure 5). The coating can withstand at least 10 000 cycles of abrasion (AATCC Test Method 8-2001), acid/base attacks, heating, and freezing. The coating also had self-healing function. After 200 abrasion cycles, the coating was able to restore the superhydrophobicity by heating treatment.

Plasma Induced Crosslinking: Liu et al.^[80] reported a durable superhydrophobic fabric prepared by pre-applying an alkyl silane (alkyl chain longer than C15) on fabric substrate, and by subsequent crosslinking treatment of the precoated fabrics with argon (Ar) plasma (Figure 6a). It was found that the Ar plasma treatment can significantly enhance Si—O—Si bonding among the silane molecules, leading to a highly crosslinked silica network. A series of alkyl silanes were tested, after the Ar plasma treatment, octadecyltrimethoxysilane (ODTMS) and HDTMS coated fabrics showed superhydrophobicity with water CA greater than 150° and SA lower than 10° as shown in Figure 6b. The coated fabrics can maintain the original superhydrophobicity after 150 cycles of washing (AATCC Test Method 61-2006) and 1000 cycles of abrasion test (ASTM D4966) (Figure 6c).

Following the same principle, Liu et al.^[81] reported a durable superamphiphobic fabric by preapplying a solution consisting of 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA), (3-glycidyloxypropyl) trimethoxysilane (GPTMS), and SNPs onto fabric substrate and by subsequent treatment with Ar plasma (Figure 7a,b). It was interesting that the coated fabric showed repellency to acetone and ethanol. It had a CA higher than 150° to the liquids with surface tension higher than 20 mN m⁻¹ (Figure 7c,d). Figure 7e shows the stability of ethanol and acetone droplets on the treated fabric. The superamphiphobic coating was very durable against repeated washing and abrasion. After 100 cycles of standard washing (AATCC Test Method 61-2006), the fabric still had CA of greater than 150° to water and hexadecane. After 2500 abrasion cycles (ASTM

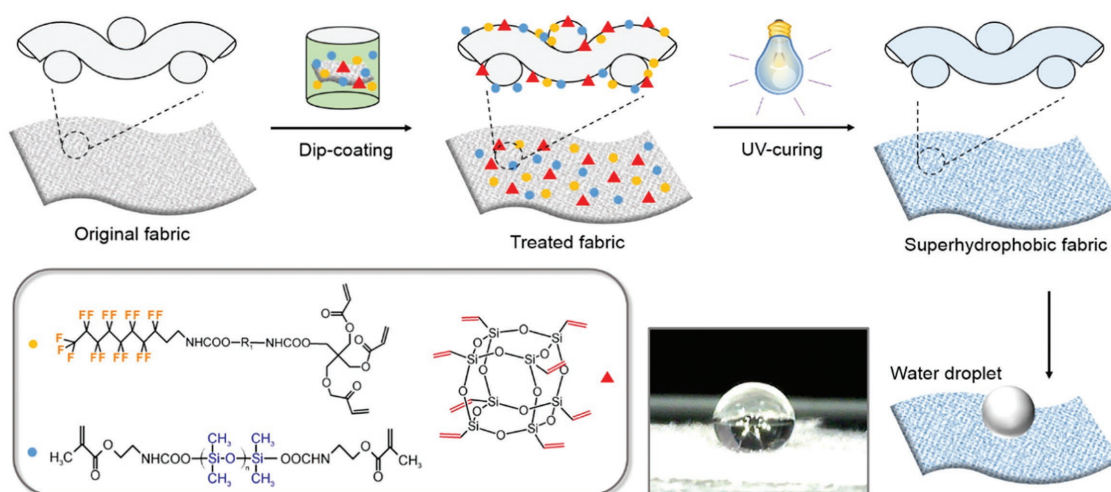


Figure 5. Schematic illustration of the fabrication of superhydrophobic cotton fabric. Reproduced with permission.^[76] Copyright 2017, Elsevier.

D4966), although the fabric was wettable by acetone and ethanol, the fabric still showed super-repellent property to hexadecane.

5.1.2. Covalent Bonding between Coating and Fiber

Forming covalent bonds between fabric substrates and coating materials is an effective way to improve the chemical/mechanical durability of SNW fabrics.^[73,82–86] It requires the substrates have chemical reactive groups, such as cotton fabrics, which the hydroxyl groups on cotton surface can form covalent bonds with the substance containing epoxide, silanol, or azide groups.

Copolymers comprising a low-surface-energy block and active group block (e.g., silanol, epoxide, azide block) were used to form a durable SNW coating on fabrics.^[20,87–90] For example, Xiong et al.^[87] used a diblock copolymer of poly-(3-(triisopropoxy)silyl) propyl methacrylate)-*block*-poly-(2-(perfluorooctyl)ethyl methacrylate) (PIPSMA-*b*-PFOEMA) to render cotton fabrics with superamphiphobic property. PIPSMA block can hydrolyze to yield silanol groups that can condense with the hydroxyl group

on cotton surface, thus forming a cross-linked covalently grafted layer on the cotton fibers. Zou et al.^[89] fabricated a durable superhydrophobic cotton by atom transfer radical polymerization (ATRP) to graft diblock copolymer of poly(glycidyl methacrylate) and poly(2,2,2-trifluoroethyl methacrylate) on cotton substrate. Since the fluorinated segments were chemically bonded to the fibers, the coated cotton showed long-term stability, and it can withstand mechanical abrasion (1000 mesh sandpaper with load pressure of 1 kg and dragging distance of 20 cm each cycle), laundering conditions (lab setup: a stirring method was applied to simulate laundering conditions), ultrasonication treatment in solvents (e.g., tetrahydrofuran, trifluorotoluene), strong acid/base aqueous (pH between 1–14), etc. Later, Zou et al.^[90] synthesized a diblock copolymer of poly(2-perfluorooctylethyl acrylate)-*block*-poly(glycidyl methacrylate-*radom-methoxy* oligoethyleneglycolyl methacrylate) (PFOEA-*b*-P(GMA-*r*-mOEGMA)) via ATRP and applied the polymer onto cotton and PET fabrics as seen in **Figure 8**. After the coating treatment, a durable superamphiphobic fabric was obtained, which was mechanically and chemically robust.

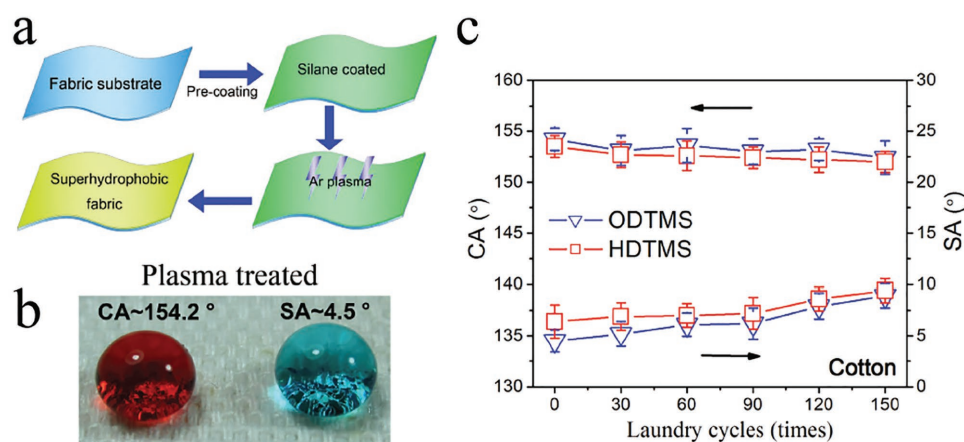


Figure 6. a) Illustration of the coating and plasma treatment procedure, b) photos of water drops on the ODTMS-coated cotton fabric surface, c) effect of washing cycles on the CA and SA of ODTMS- and HDTMS-treated cotton fabrics. Reproduced with permission.^[80]

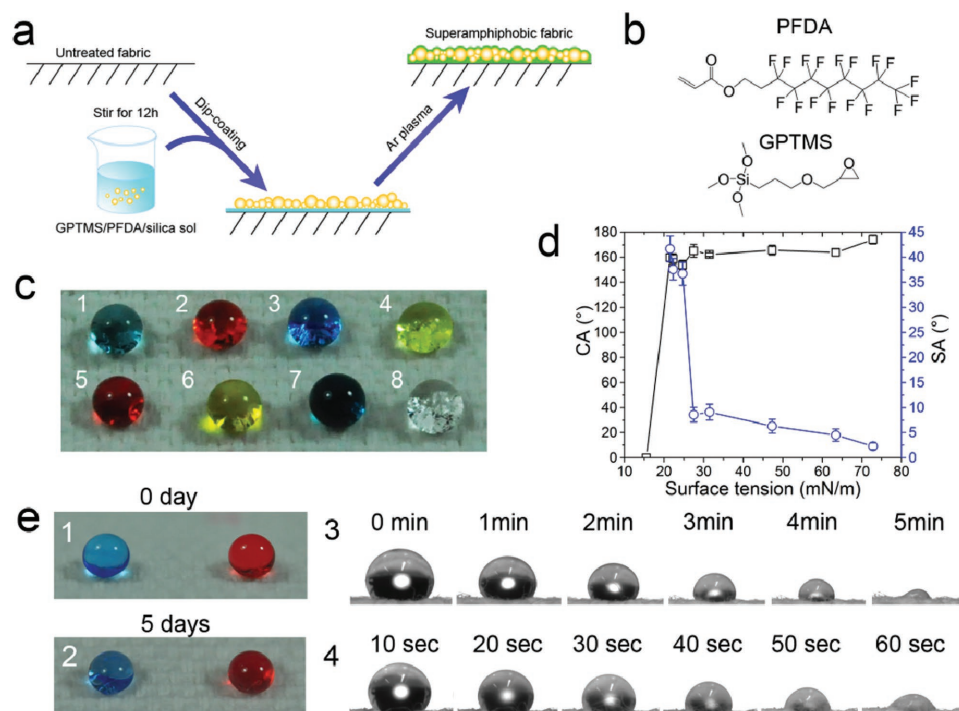


Figure 7. a) Illustration of the treatment procedure. b) Chemical structures of PFDA and GPTMS. c) Photo of colored liquid drops on treated cotton surface: 1) water, 2) silicone oil, 3) hexadecane, 4) ethanol, 5) soybean oil, 6) ethylene glycol, 7) glycerol, 8) acetone (10 μL for each drop; the small amount of dye used had no influence on the contact angles). d) Dependency of CA and SA on the surface tension of liquids. e) Liquid drops (blue-colored hexadecane and red-colored soybean oil) on treated cotton fabric for different time periods: 1) 0 d, 2) 5 d; variation of liquid drops with time: 3) ethanol, 4) acetone. Reproduced with permission.^[81]

Free radical induced graft-polymerization was also used to prepare durable superhydrophobic coating on fabrics. Under γ -ray radiation, polymerization took place and covalent bonds formed between cotton and low surface energy compounds to enhance the adhesion.^[20,73,82,91] Yu et al.^[83] reported a method to covalently immobilize TiO_2 nanoparticles onto cotton fabric

using a monomer to form a graft chain network that involved TiO_2 nanoparticles (**Figure 9**). First, C=C bonds were introduced onto the surface of TiO_2 nanoparticles. Second, the modified TiO_2 nanoparticles and 2-hydroxyethyl acrylate (HEA) were cografed onto cotton surface under γ -ray radiation. The coated fabric exhibited superhydrophobicity and can withstand at least 30 laundering cycles (AATCC Test Method 61–2006, 2A), which was equivalent to 150 instances of home laundings.

Moreover, metal alkoxides that can hydrolyze and condense with hydroxyl groups were used to fabricate durable coatings on cotton surfaces.^[92,93] Singh et al.^[93] fabricated durable superhydrophobic cotton fabric by coating the cotton with in situ synthesized zirconia sol and subsequently by surface modification with HDTMS and stearic acid for hydrophobization and with cetyltrimethyl ammonium bromide (CATM) and silver nitrate (AgNO_3) for photocatalytic activity. The Zirconium can condense with hydroxyl groups on cotton fabric and silanol group from HDTMS, thus resulting in a strong bonding among HDTMS, zirconia, and cotton fabric. Further modification with CATM/ AgNO_3 rendered the fabric with photocatalytic activity. The coated cotton fabric can withstand 30 times of sandpaper abrasion (1500 mesh, 100g of loading), long-hour

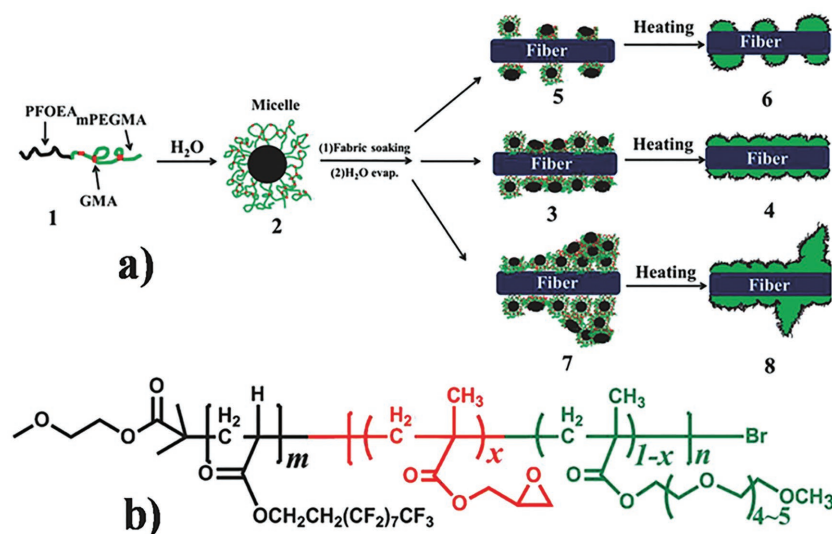


Figure 8. a) Process for coating treatment of fabric and the possible coating structures. b) Chemical structure for PFOEA-*b*-P(GMA-*r*-mOEGMA). Reproduced with permission.^[76] Copyright 2017, Elsevier.

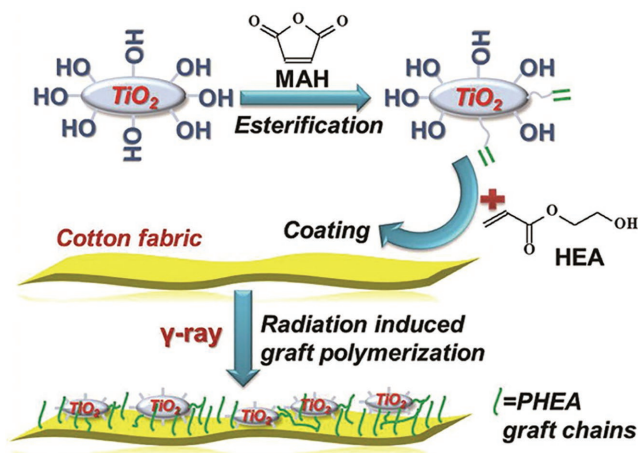


Figure 9. Procedure of γ -ray irradiation induced covalent immobilization of TiO_2 nanoparticles on cotton fabric. Reproduced with permission.^[83] Copyright 2013, American Chemical Society.

UV irradiation, and acid and base (pH between 2–12) attacks. Silane coupling agents were also used as heterogeneous grafting chemicals to improve the adhesion between cellulose fiber and silica layer.^[21,86,94,95] Xu et al.^[94] synthesized silica clusters functionalized with epoxy and amino groups, respectively. The modified silica clusters were then immobilized alternately onto the chitosan pretreated cotton fabrics through epoxide-amino reaction, after functionalized with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTMS), a durable superamphiphobic coating was formed on the cotton fabrics as shown in Figure 10. The coated cotton showed CA of 164.4° and 156.3° to water and hexadecane. This coating was durable against

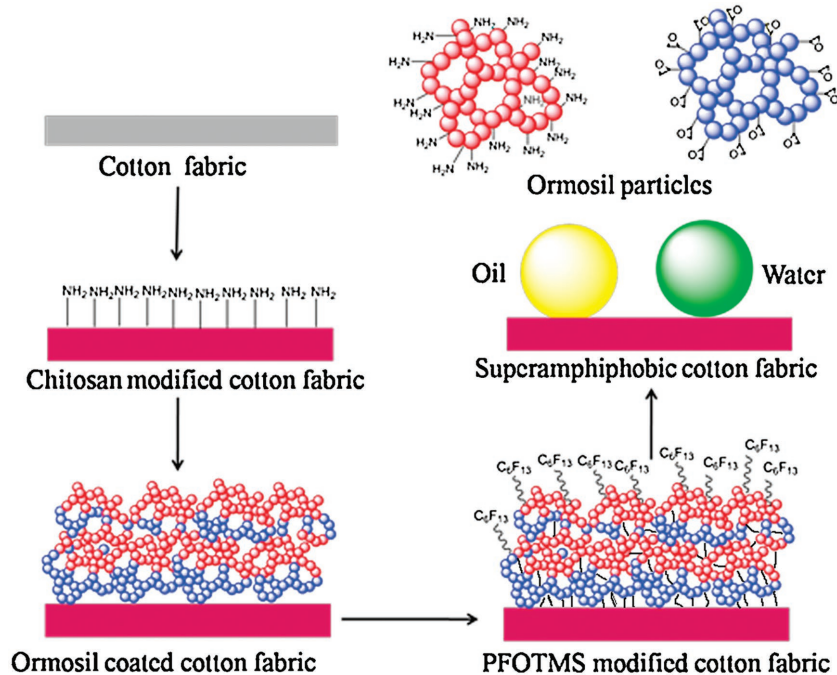


Figure 10. Schematic diagram of the fabrication process for superamphiphobic cotton fabrics. Reproduced with permission.^[94] Copyright 2015, Elsevier.

10 000 cycles of abrasion (Martindale Method, ASTM, D49667), 30 cycles of machine washing (AATCC Test Method 61-2006), and 98% H_2SO_4 attack.

Synthetic fabrics such as polyester fabrics have little reactive groups on surfaces. To build a chemical bonds and robust hierarchical structures on fibers, pretreatment such as alkali etching and plasma texturing was employed.^[85,96–100] Xue et al.^[85,96–99] fabricated durable superhydrophobic polyester fabrics through chemical etching of fiber surfaces and subsequent modification of low surface energy fluoro-containing materials onto the roughened fibers. As shown in Figure 11a, the cleaned PET was first immersed in a specific concentration of sodium hydroxide solution (NaOH) for chemical etching to obtain abundant hydroxyl groups (Figure 11b). Then α -bromoisobutyl bromide (BiBB) as the ATRP initiator was used to immobilize the Br group on the etched PET fabric surface. The fluorinated methacrylate polymer finally grafted on the PET-Br and the resultant fabric was denoted as PET-g-P(TFEMA) (Figure 11c). The obtained superhydrophobic fabrics exhibited excellent chemical stability even after long-hour exposure to different chemicals, such as acid, base, salt, acetone, and toluene. The coated fabrics maintained superhydrophobicity after 100 laundering cycles (Figure 11d, AATCC Test Method 61-2003 No 1A), 2500 abrasion cycles (Figure 11e, AATCC Test Method 8-2001), long time exposure to UV irradiation. Moreover, the coating showed excellent antifouling properties. Another work by Oh et al.^[100] reported a durable superhydrophobic PET fabric prepared by selective oxygen plasma etching, followed by a heating process (Figure 12a). Oxygen plasma etching provided the fibers with hierarchical surface roughness (Figure 12d,e), and also introduced the polar groups containing oxygen groups, thus the fabric showed superhydrophilic property with WCA of 0° as seen the insert photo in

Figure 12e. The subsequent heating process accelerates the migration of polar groups into the fabric, which resulted in a superhydrophobic recovery on the plasma-etched PET fabric. The obtained superhydrophobic fabric can maintain the superhydrophobicity after repeated tap test (ASTM D3359 with a Scotch Tap) and acid and base (pH values in the range between 1 and 11) attacks.

5.1.3. Mussel-Inspired Polydopamine

The bioadhesion of marine mussels has drawn great interest in the last decades. Mussels can attach to virtually all types of inorganic and organic surfaces, including classically adhesion-resistant materials such as poly(tetrafluoroethylene) (PTFE).^[101,102] The reason for these unique outstanding adhesion properties is a really complex protein mixture containing 25–30 different mussel foot proteins that are expressed and excreted by the mussel to form the so-called adhesive byssus.^[103] In 1981, Waite and Tanzer first identified 3,4-dihydroxyphenyl-L-alanine (DOPA) and claimed its key role in

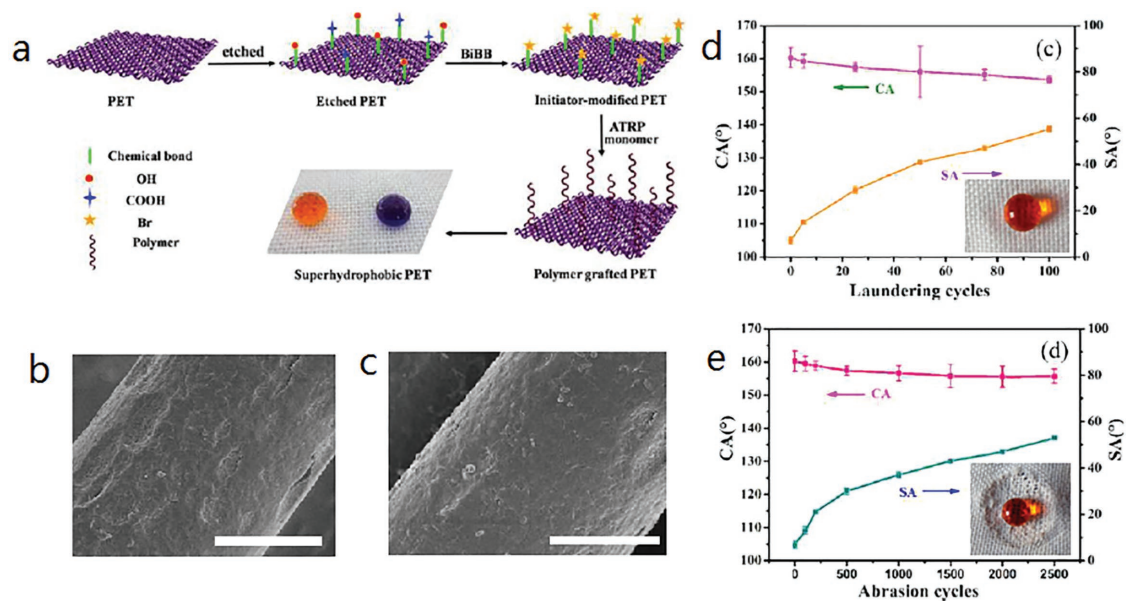


Figure 11. a) Schematic illustration of the fabrication of superhydrophobic fabrics, b) SEM image of NaOH etched fabric, c) SEM image of PET-g-P(TFEMA) fabric, d) Changes of CA and SA of PET-g-P(TFEMA) fabric with washing cycles, insert photo shows the red water droplet on the coated fabric after 100 cycles of washing test, e) Changes of CA and SA of PET-g-P(TFEMA) fabric with abrasion cycles, insert photo shows the red water on the coated fabric after 2500 times abrasion test. (SEM scale bars are 5 μ m). Reproduced with permission.^[99] Copyright 2015, American Chemical Society.

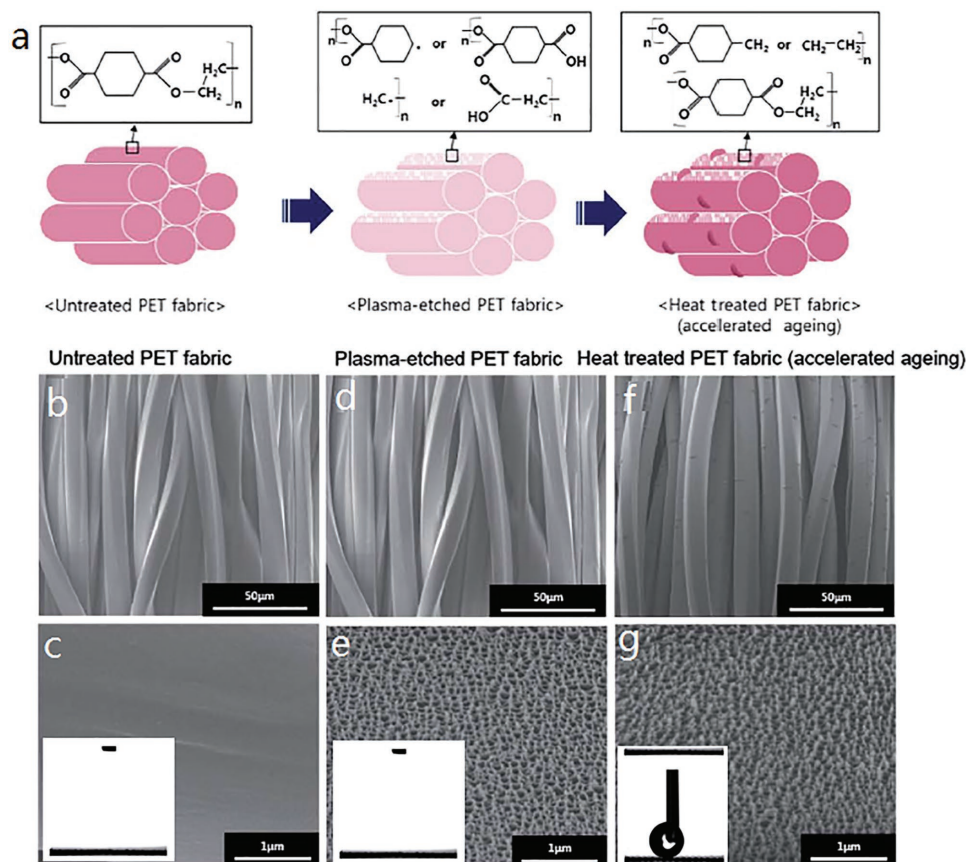


Figure 12. a) Schematic illustration showing the coating procedure, b–g) SEM images and insert photos of static contact angles for (b,c) uncoated PET, (d,e) 60 min plasma etched PET fabric, and (f,g) plasma etched and heated at 130 °C for 24 h PET fabric. Reproduced with permission.^[100] Copyright 2017, Royal Society of Chemistry.

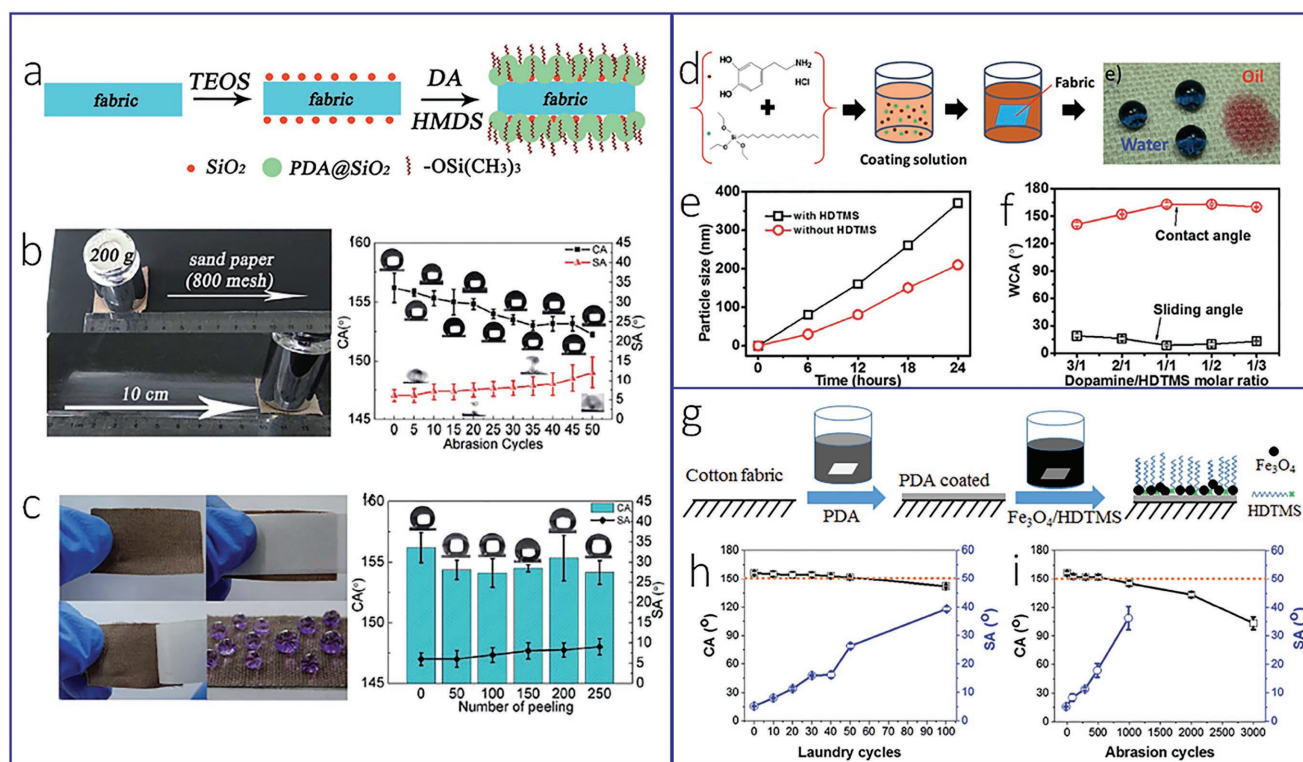


Figure 13. a) Schematic of the preparation of superhydrophobic PDA@SiO₂ coated cotton fabric, b) the photo showing the abrasion process and the figure of CA and SA change of the coated fabric after tear test cycle, the insert photos showed the static water droplets (5 μ L) after each cycle. a-c) Reproduced with permission.^[109] Copyright 2017, Royal Society of Chemistry. d) Chemical structure of dopamine and HDTMS, and coating procedure, the digital photo shows water and cooking oil on the coated cotton fabric, e) PDA particle size change with time, f) the effect of dopamine/HDTMS molar ratio on the water contact angle and sliding angle of HDTMS/water coated cotton fabric. d-f) Reproduced with permission.^[110] Copyright 2017, Royal Society of Chemistry. g) Schematic illustration of the procedure for preparing superhydrophobic cotton fabric, h, i) CA and SA change of the coated fabric with h) laundry cycles, and i) abrasion cycles. g-i) Reproduced with permission.^[61] Copyright 2018, Royal Society of Chemistry.

the adhesion mechanism.^[104] Inspired by the adhesive proteins secreted by mussels, in 2007, Lee et al.^[105] used dopamine self-polymerization to form a thin, strong surface-adherent PDA films on a wide range of inorganic and organic materials. Some researchers have reported that PDA can easily form nanoparticles and aggregates on substrates after deposition, which may help to roughen substrates to meet the topological requirements of SNW surfaces. In recent years, PDA has been used, combining biomimetic principles, to obtain durable superhydrophobic coatings on fabrics.^[61,106–110] Guo et al.^[109] designed a robust and boiling water-resistant superhydrophobic cotton through copolymerization reaction and trimethyl silyl modified process at room temperature. Briefly, silica particles were firstly obtained from the hydrolysis reaction of tetraethoxysilane (TEOS), the hydrolysis product HO-Si(CH₃)₃ of 1,1,1,3,3,3-hexamethyl diisilazane (HMDS) can be reacted with rest of the -Si-OH groups on the surface SiO₂. Moreover, PDA was fabricated from dopamine self-polymerization in water under alkali condition. The obtained PDA can adhere to silica to form micro/nanoscale PDA@SiO₂ aggregations (Figure 13a). The PDA@SiO₂ can also adhere to the fiber surface. The resultant superhydrophobic fabric exhibited not only great resistance to mechanical abrasion (Figure 13b,c; 800 mesh sandpaper with load pressure of 200 g and dragging distance

of 10 cm), wear and ultrasonic treatment but also had excellent superhydrophobicity stability toward UV irradiation, high temperature (200 °C 2 h) and organic solvents immersion (e.g., ethanol, acetone, n-hexane, and DMF). In addition, the coated fabric can withstand boiling water without losing the original superhydrophobicity. Wang et al.^[110] in our group proved that codeposition of dopamine with an alkyl silane, hexadecyl trimethoxysilane (HDTMS) in neutral aqueous solution rendered fabrics (cotton, polyester, wool, etc.) with a durable superhydrophobic surface (Figure 13d). In this work, DA was dissolved in deionized water, HDTMS was then added in the DA solution to form a homogeneous DA/PDA/HDTMS coating solution, which can be directly applied onto the fabric through dip-coating technique. The resultant fabrics showed durable superhydrophobic property with water CA of 163° and SA of 8.6° (Figure 13e,f). After 20 washing cycles (AATCC 61-2006, 2A) and 500 cycles of abrasion (Martindale, ASTM D4996), the coated fabric still maintained the superhydrophobicity. Recently, Fu et al.^[61] fabricated a multifunctional cotton fabric showing durable superhydrophobicity and magnet responsive property using PDA, Fe₃O₄ nanoparticles and hexadecyltrimethoxysilane as coating materials. This coating is water-based and fluoride free (Figure 13g). The coated fabric exhibited a fast magnetic responsivity and water CA of 156°. In addition, the coating is

durable enough to withstand at least 50 cycles of laundering (AATCC 61-2006, 2A) and 500 cycles of Martindale abrasion (Martindale, ASTM D4966) without losing its original superhydrophobicity (Figure 13h,i).

PDA was normally fabricated from DA under alkali condition, and can form a durable coating on different fabrics. However, coatings prepared from PDA are known to have a dark appearance. Thus the coated fabrics are either in dark or light brown.

5.2. Physical Methods

5.2.1. Elastomeric Nanocomposite

Elastomers are facile materials that can form a durable functional coating on fabrics. By incorporating inorganic nanoparticles (e.g., SiO₂, TiO₂, and ZnO) or carbon nanotubes into elastic polymers, the toughness can be improved largely. The composite may not involve covalent bond and chemical reactions between the coating materials and the substrates. However, nanocomposite coating can be widely applied on various solid substrates (e.g., fabrics, sponge, wood, glass, and metal). The compatibility of nanoparticles and polymers is a prerequisite for the selection of coating materials. Some research studies developed durable superhydrophobic fabric coating through nanocomposite coating technique,^[111–117] such as a fluorinated acrylic polymer/silica nanoparticles nanocomposite coating,^[114] an oligomer of hexadecyltriethoxysilane (HDTES) and HDTES-modified silica nanoparticles nanocomposite coating,^[112] PDMS/SiO₂-TiO₂ nanocomposite coating.^[113] This method has been also used for developing durable superamphiphobic fabric coating in recent years.^[118–120]

Our research group successfully developed different elastomer polymer/nanoparticle nanocomposite coatings to prepare durable superhydrophobic and superamphiphobic fabrics.^[22,23,120] By mimicking the car tires, a classic nanocomposite, in 2012, Zhou et al.^[22] used polydimethylsiloxane (PDMS), incorporating with fluorinated alkyl silane modified silica nanoparticles, to prepare a durable superhydrophobic coating on fabrics. The coated fabric exhibited superhydrophobicity with water CA of 171° and remarkable durability against many severe damages, e.g., 500 cycles of machine washing (500 cycles, AATCC 61-2001, 2A), 28 000 cycles of abrasion (Martindale Method, ASTM D4966), boiling water, strong acid (pH 1), and alkali (pH 14) attacks, without changing the superhydrophobicity. Later, Zhou et al. reported durable superamphiphobic fabric coatings using a elastomer polymer PVDF-HFP and 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane. The SNW property can be improved by either using silica nanoparticles,^[23] or generating a rough PVDF/FAS coating by using highly volatile solvent.^[15] The coatings were all durable against at least 600 cycles of washing (AATCC 61-2006), 8000 cycles of abrasion (ASTM D4966), strong acid (pH 1) and base attacks (pH 14), and boiling. Recently, Zhou et al.^[120] proved that lyophobic nanoparticles, fluorinated alkyl silane (FAS), and fluorocarbon copolymer can form a stable dispersion in water. Such a stable dispersion was suitable for preparing durable superamphiphobic surfaces on various solid substrates (e.g., fabrics, sponge, wood, glass, and metal) (Figure 14a,b). The

coated substrates showed superamphiphobicity with low contact angle hysteresis. The coating is durable enough against physical abrasion (ASTM D4966), repeated washing (AATCC 61-2006), boiling in water, and strong acid/base attacks (Figure 14c,d).

5.2.2. Nonelastomeric Nanocomposite

Without using elastomeric polymers, some nanocomposite coatings used to prepare superhydrophobic fabrics were prepared by mixing nanoparticles in solvents to form a coating suspension.^[116,121] Lu et al.^[116] reported an ethanol suspension comprising perfluorosilane-coated TiO₂ nanoparticles that can be applied onto various substrates to form a self-cleaning surfaces. The coating layer was adsorbed physically on the substrates. The coated substrates exhibited self-cleaning property no matter when exposed to air or oil. Although the coated glass slide can withstand 40 cycles of abrasion damages without losing the superhydrophobicity, the washing durability and abrasion durability of the coated fabrics were not reported.

Li et al.^[121] used a nanocomposite suspension to prepare durable superhydrophobic fabrics through dip-coating in the PFW/GF suspension. Briefly, a mixture of polyfluorowax (PFW) and graphite fluoride (GF) was added to a solvent mixture of ethanol, acetone, and ethyl acetate to form a stable suspension. The coated fabric showed water CA of 157.7°. This superhydrophobic function did not influence further dyeing of the fabric. The coating can endure more than 600 cycles of sandpaper abrasion (1000 mesh) and showed long-term stability at extreme conditions, such as 50 h UV exposure, very low (−18 °C) and very high (160 °C) temperature, strong acid (pH 2) and alkali (pH 12) solution.

6. Self-Healing SNW Fabrics

Inspired by the self-healing superhydrophobicity of living plants, many different synthesis strategies have been developed to fabricate self-healing SNW materials.^[122–133] In 2010, Li et al.^[122] for the first reported a self-healing superhydrophobic coating that was prepared by chemical vapor deposition (CVD) of a fluoroalkyl silane (FAS) on a layer-by-layer assembled porous surface, and the self-healing function was derived from the reacted FAS embedded in the rigidly flexible coating layer. In 2011, Wang et al.^[134] from our group first reported a self-healing superamphiphobic coating on fabric substrates (e.g., cotton, polyester, wool) using FD-POSS and FAS as coating materials. When the coating was damaged chemically by plasma or strong alkali for instance, the fabric turned hydrophilic with CA of 0° to both water and oil. However, when the damaged fabric was heated for a short time, the original superamphiphobicity was restored. Since then, considerable works have been devoted to fabrication of self-healing SNW fabrics. However, the current self-healing approaches have only been applied on superhydrophobic and superamphiphobic surfaces. Self-healing function on other SNW surfaces such as SHI-SOP and U-SOP have not been reported.

In recent years, different strategies have been developed to fabricate SNW fabrics with self-healing function. In this section, we discuss in detail about the types and fabrication

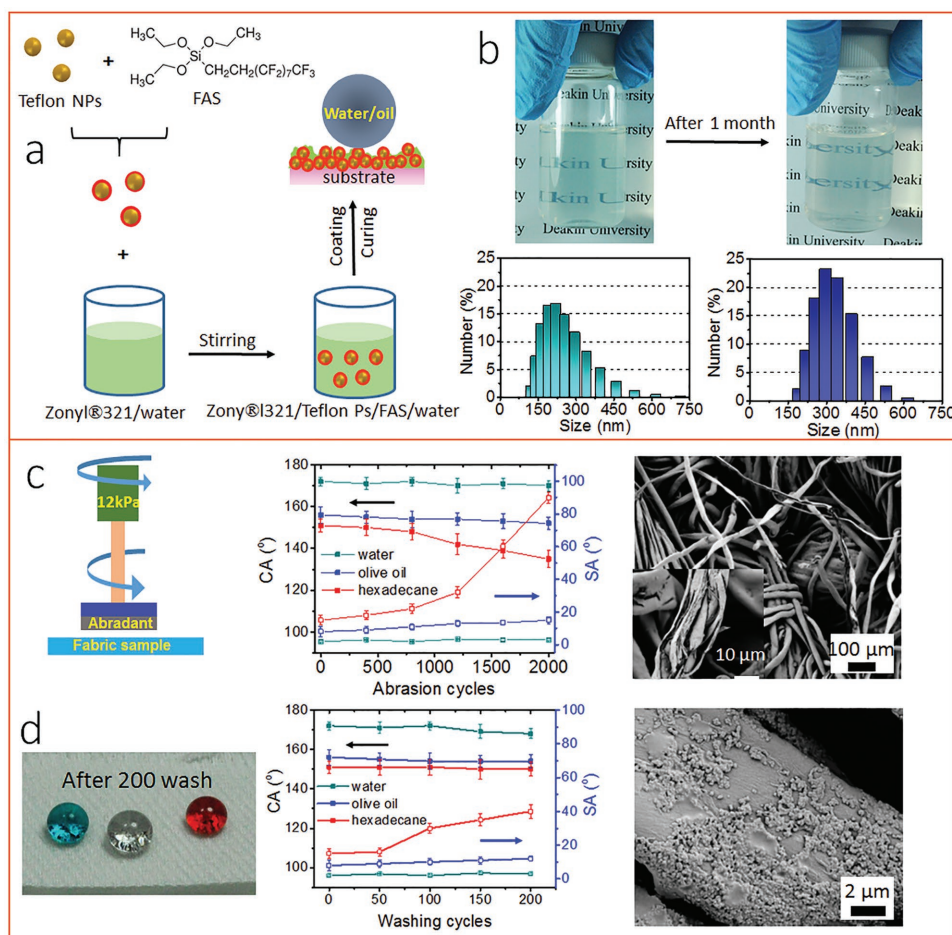


Figure 14. a) Schematic illustration of the procedure for solution preparation and coating treatment. b) Photos showing the coating solution before and after one-month storage at room temperature and corresponding histogram of size distribution in the solutions. c) Schematic illustration of Martindale abrasion test on fabric, CA and SA change with abrasion cycles on the coated cotton fabric, and SEM images of coated cotton after 2000 abrasion cycles (the insert is the enlarged image of a broken fiber). d) Blue water, clear olive oil, and red hexadecane droplets on the coated cotton after 200 washing cycles, CA and SA change with washing cycles of the cotton fabric, and SEM image of the cotton fabric after 200 washing cycles. Reproduced with permission^[120]

approaches of the self-healing SNW fabrics and the characterization methods.

6.1. Restoration of Low-Surface-Energy Components

This is the most commonly used strategy to prepare self-healing SNW fabrics. An excess amount of low-surface-energy components is embedded into rough matrix with micro- and nanoscaled structures. Once the wettability on the coated surface become decomposed or degraded, the SNW can be restored by migration/rotation/recrosslinking of the low-surface-energy molecules to the damaged surface (see Figure 15). So far, all the reported SNW fabrics with self-healing ability are based on restoration of low-surface-energy molecules in response to either temperature, humidity, or light. Details of the reported SNW fabrics with self-healing property by restoration of low-surface-energy molecules are listed in Table 5.

It can be seen that FD-POSS and FAS were applied as healing agents in most approaches for preparation of

self-healing SNW coatings on fabrics. All the works on self-healing superamphiphobic fabrics used either FD-POSS or FAS or both to lower the surface free energy and heal the coating when the coating surface was damaged chemically or physically.^[15,23,25,26,120,131,134–136] Due to the safety concern of using long-chain fluoro-containing, some research groups developed fluoro-free coating systems to prepare self-healing superhydrophobic fabric coatings.^[78,110,137,138] For example, Liu et al.^[137,138] used polydopamine@octadecylamine (PDA@ODA) nanocapsules to treat fabrics, where ODA with low-surface-energy acted as healing agent, and PDA nanocapsules with high adhesion strength acted as a container for storing ODA and provided roughness on coating surfaces. The coated fabrics exhibited self-healing ability against chemical and physical damages, when the fabric surface was damaged and lost the superhydrophobicity, ODA molecules can migrate to the surface and restore the original liquid repellency. The migration of ODA can be triggered by heating at high temperature or short time irradiation with near-infrared light. Later, Xue et al.^[78] developed a self-healing superhydrophobic coating system containing PDMS and ODA on fabrics. The coating

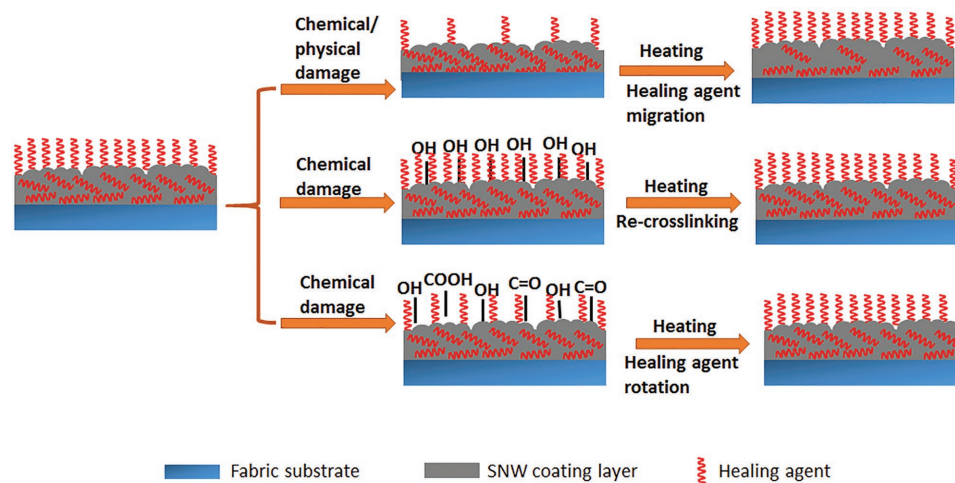


Figure 15. Schematic of the possible self-healing processes for a SNW coating after physical or chemical damages.

was durable to withstand repeated washing and abrasion. When the coating surface was damaged chemically, the migration of ODA can be introduced to recover the surface superhydrophobicity under heating or room condition. Recently, Wang et al.^[110] developed a water-based fluoro-free coating system to prepare durable self-healing superhydrophobic fabrics using dopamine (DA), PDA, and HDTMS as coating materials. HDTMS with low-surface energy was used as healing agent. When the coating was damaged chemically, HDTMS can migrate to the surface to restore the superhydrophobicity under heating treatment.

For most of the self-healing SNW fabrics, the migration of low-surface-energy components was triggered by temperature. It was found that the migration of FD-POSS can be also triggered by moisture (RH, 35%), and the healing process can be accelerated in a more humid environment or at higher temperature.^[139] ODA was used as a healing agent in self-healing superhydrophobic fabric coatings, apart from heating-triggered self-healing (40 °C–80 °C, 20 min), an accelerated migration of ODA can be also triggered by short time near-infrared (NIR) laser (40 s).^[138]

Wu et al.^[91] reported a strategy to fabricate self-healing superhydrophobic cotton fabric by radiation-induced graft polymerization of hexyl methacrylate and lauryl methacrylate (PHMA/PLMA). When the surface was damaged physically, the migration of PHMA/PLMA with low-surface energy can be realized by steam ironing at 200 °C to restore the original superhydrophobicity.

6.2. Topographic Change

Most of the developed self-healing coating systems realized the self-healing ability by minimizing the surface energy via migrating/releasing of the embedded healing agents from the inside of coating structure to the surface. However, restoring the SNW property by regeneration of topographic structures was reported in recent years by only a few research works.^[140,141] Wang et al.^[26] from our group reported a durable

superamphiphobic fabric with self-healing ability against both physical and chemical damages using FAS modified silica nanoparticles, FAS, and FD-POSS as coating materials via wet-chemical coating technique (Figure 16a). When the superamphiphobic coating was damaged chemically (e.g., vacuum plasma treatment, 5 min) or physically (e.g., blade scratching, sandpaper abrasion), the fabric turned amphiphilic with CA of 0° to both water and oil. However, when the damaged fabric was heated at 140 °C for 5 min, the original superamphiphobicity can be recovered (Figure 16b,c). The mechanism of self-healing against chemical and physical damages was attributed to the movement of coating on the fabric substrates. Figure 16f,g shows the SEM images of the coated fiber after 100 cycles of blade scratches, and after being heated at 140 °C for 5 min. The coated fibers became smoother after scratching and in some areas the nanoparticles protrusion of the surface structure was removed completely, the reduction in surface roughness resulted in the decreased repellency. After the heating treatment, however, the surface topography changed (see SEM image). At high temperature, the coating became more mobile and melted. Further cooling to the room temperature resulted in solidification of the coating layer with the scratch being completely healed.

Li et al.^[140] fabricated a self-healing superhydrophobic modification on cotton fabrics via immersing the fabrics into 3-aminopropyltriethoxysilane solution followed by polymerization treatment of styrene. The coated PS-grafted fabrics showed superhydrophobic property with WCA greater than 150°. When the coating was damaged physically by immersing in poor solvent (70 °C, 8 h, in water) or 30 cycles of abrasion damage, the surface roughness increased, and the WCA reduced to 0°, however, when immersing the damaged fabrics in toluene at 70 °C for 4 h, or giving heat simulation at 110 °C, the relatively smooth morphology was resulted and WCA was recovered as over 150°. Huang et al.^[141] developed an abrasion-triggered durable superhydrophobic fabrics. When abrasion was applied, the hierarchical fibrils increased roughness in microscale on the abraded area because of splitting fiber bundles, which self-healed the superhydrophobicity.

Table 5. SNW fabrics with self-healing function based on restoration of low-surface-energy components.

Approach	Substrate	Method	Wetting property	Healing agents	Self-healing ability	Self-healing evaluation and main results	Refs.
Temperature-triggered self-healing	Polyester, cotton, wool	Dip coating the fabrics in an ethanol solution containing FD-POSS and FAS	Superamphiphobic; WCA $\approx$ 171°, OCA > 150° for liquids with $\gamma > 26.5 \text{ mN m}^{-1}$	FD-POSS	Against chemical damages	WCA&OCA turned 0° after plasma or KOH (pH 14) etching, after heating at 135 °C for 3 min, the superamphiphobicity was restored.	[134]
	Polyester	Two-step coating: 1) Dip coating the fabrics in hydrophobic SiO ₂ NPs solution; 2) Dip-coating the SiO ₂ coated fabrics in FD-POSS/FAS solution	Superamphiphobic; WCA $\approx$ 171°, OCA > 150° for liquids with $\gamma > 22.1 \text{ mN m}^{-1}$	FD-POSS/FAS	Against both chemical & physical damages	Chemical damage: WCA&OCA turned 0° after plasma etching, the superamphiphobicity can be restored after heating at 140 °C for 5 min. Physical damage: WCA&OCA reduced to <150° and <120°, respectively, after scratching with a sharp blade, sandpaper abrasion, and Martindale abrasion, after heating at 140 °C for 30 min, the superamphiphobicity was recovered.	[25]
	Polyester	Two-step coating: 1) Dip-coating the fabrics in FeCl ₃ /FAS/FD-POSS solution; 2) Subsequently treated with EDOT vapor.	Superamphiphobic; WCA $\approx$ 169°, OCA > 156° for liquids with $\gamma > 27.5 \text{ mN m}^{-1}$	FD-POSS/FAS	Against chemical damages	WCA&OCA turned 0° after plasma etching, after heating at 135 °C for 5 min or at RT for 24 h, the superamphiphobicity was restored.	[26]
	Cotton	Dip coating the fabrics in V-PDMS/TV-PFOD/OV-POSS, followed by UV-curing treatment.	Superhydrophobic; CA > 150° to deionized water, tea, orange juice, mild, coffee, cola.	FD-POSS/FAS	Against physical damages	WCA reduced to $\approx$ 120° after 20 cycles of abrasion (load pressure was 500 g), after heating at 100 °C for 5 min, the WCA reached to 150° again.	[76]
	Polyester	Dip coating the fabrics in acetone solution containing T-FAS and FOTS.	Superhydrophobic & oleophobic, CAs were 167°, 157°, and 148° to water, ethylene glycol, and peanut oil.	T-FAS/FAS	Against physical & chemical damages	Physical damage: after 100 abrasion cycles with a load pressure of 45 kPa, CA to peanut oil reduced to 95°, after heating at 135 °C for 10 min, the CA was restored to 143°. Chemical damage: CAs reduced to 128°, 90°, and 0° for water, ethylene glycol, and peanut oil after immersing in KOH (pH 14) for 12 h, after rinsing and heating at 135° for 10 min, the original superhydrophobicity was restored.	[168]
	Polyester, cotton, wool	Two step coating: 1) Dip coating in hydrophobic SiO ₂ sol; 2) Dip coating in PVDF-HFP/FAS solution.	Superamphiphobic, WCA $\approx$ 172°, OCA > 160° for liquids with $\gamma > 27.5 \text{ mN m}^{-1}$.	FAS	Against chemical damage	WCA&OCA turned to 0° after plasma etching, the superamphiphobicity can be restored after heating at 135 °C for 5 min or at RT for 24 h.	[23]
	Polyester, cotton, wool	Dip coating the fabrics in a mixture of acetone/DMF containing PVDF-HFP and FAS	Superamphiphobic, WCA $\approx$ 162°, OCA > 160° for liquids with $\gamma > 21.5 \text{ mN m}^{-1}$	FAS	Against chemical damage	After 90 min UV irradiation, CAs reduced to 92°, 32°, and ° to water, olive oil, and silicon oil. After heating at 135 °C for 5 min, the superamphiphobicity was recovered.	[15]
	Woven & nonwoven fabrics	Dip coating the fabrics in a waterborne Teflon NPs/Zonyl321/FAS solution.	Superamphiphobic, WCA $\approx$ 172°, OCA > 151° for liquids with $\gamma > 27.5 \text{ mN m}^{-1}$	FAS	Against chemical & physical damages	Chemical damage: WCA & OCA became 0° after plasma treatment, and the superamphiphobicity can be restored after heating at 135 °C for 10 min. Physical damage: After 1200 cycles of Martindale abrasion (loading pressure of 12 kPa), the CA reduced to 142° for hexadecane, after 10 min heating at 135 °C, the CA was back to 151°.	[120]
	Polyester	Spraying coating the substrates by combination of PAL, PFDTS, and TEOS coating solution.	Superamphiphobic, WCA $\approx$ 165°, OCA > 153° for liquids with $\gamma > 21.6 \text{ mN m}^{-1}$	FAS	Against chemical damage	Both WCA&OCA became 0° after plasma etching, the original superamphiphobicity returned after storing at RT for 24 h.	[131]
	Cotton	Dip coating the fabrics in PFW/GF in a mixed solvent of ethanol/acetone/ethyl acetate	Superhydrophobic, WCA $\approx$ 157°	PFW/GF	Against chemical damage	After plasma treatment, the fabric turned superhydrophilic, after heating at 110 °C for 3 min, the superhydrophobicity was restored.	[121]

Table 5. Continued.

Approach	Substrate	Method	Wetting property	Healing agents	Self-healing ability	Self-healing evaluation and main results	Refs.
	Cotton	Dip coating the fabrics in PDA/ODA coating solution.	Self-cleaning, CAs were 145°, 140°, 138°, 142° for water, juice, coffee, and milk. WSA < 10° for these liquids	ODA	Against chemical damage	The fabrics turned hydrophilic after plasma etching, after heating at 80 °C for 20 min, the self-cleaning property was restored.	[137]
	PET	Dip coating the fabrics in PDMS/ODA solution	Superhydrophobic, WCA = 160°, WSA = 6°	ODA	Against chemical damage	WCA reduced to ≈50° after plasma etching, after heating at 40 °C for 20 min or at RT for 12 h, the original superhydrophobicity was restored.	[78]
	Cotton, polyester, wool	Dip coating the fabrics in DA/PDA/HDTMS coating solution	Superhydrophobic, WCA = 163°, WSA = 8.6°	HDTMS	Against chemical damages	WCA turned 0° after plasma, acid (pH < 4), and base (pH > 12), after heating at 140 °C for 10 min, the superhydrophobic property was restored.	[110]
	Cotton	Dip coating the fabrics in PLMA/PHMA solution	Superhydrophobic, WCA > 150°	PHMA/PLMA	Against physical damage	The coating can survive at least 24 000 abrasion cycles (a load of 44.8 kPa) with periodic steam ironing at around 200 °C	[91]
Relative humidity-triggered (RH)	Cotton	Two step coating: 1. Dip coating in APP/bPEI; 2. dip coating in F-POSS	Superhydrophobic, WCA = 160°, WSA = 4°.	FD-POSS	Against chemical damage	WCA became 0° after plasma etching, after storing in RH (35%) for 1 h, the original superhydrophobicity was regained.	[169]
	Cotton	Coating the fabrics in sequence with PEI, AgNPs, and F-POSS	Superhydrophobic, WCA = 169°, WSA = 3°.	FD-POSS	Against chemical damage	WCA became 0° after plasma etching, after storing in RH (55%) for 30 min, the original superhydrophobicity was regained. The healing process can be accelerated by increasing the RH and temperature.	[139]
Light irradiation-triggered	Cotton	Dip coating the fabrics in PDA/ODA/Fe ₃ O ₄ .	Superhydrophobic, WCA = 152°.	ODA	Against chemical damage	WCA became 0° after plasma etching, after 808 nm near-infrared (NIR) laser (0.55 W cm ⁻²) for 40 seconds, the original superhydrophobicity was regained.	[138]

*WCA, water contact angle; OCA, oil contact angle; FAS, 1H,1H,2H,2H-perfluorodecyltriethoxysilane (C₁₆H₁₉F₁₇O₃Si); T-FAS: thiol-ene fluoroalkyl siloxane; NPs, nanoparticles; FD-POSS, fluorinated-decyl polyhedral oligomeric silsesquioxane; EDOT: 3,4-ethylenedioxythiophene; V-PDMS: vinyl-terminated polydimethylsiloxane; TV-PFOD, tri-functionality vinyl perfluoro decanol; OV-POSS, octavinyl-POSS; PVDF-HFP, poly(vinylidene fluoride-hexafluoropropylene); PAL, palygorskite; TEOS, tetraethoxysilane; PFW, polyfluorowax; GF, graphite fluoride; DA, dopamine; PDA, polydopamine; ODA, octadecylamine; HDTMS, hexadecyl trimethoxysilane; RT, room temperature

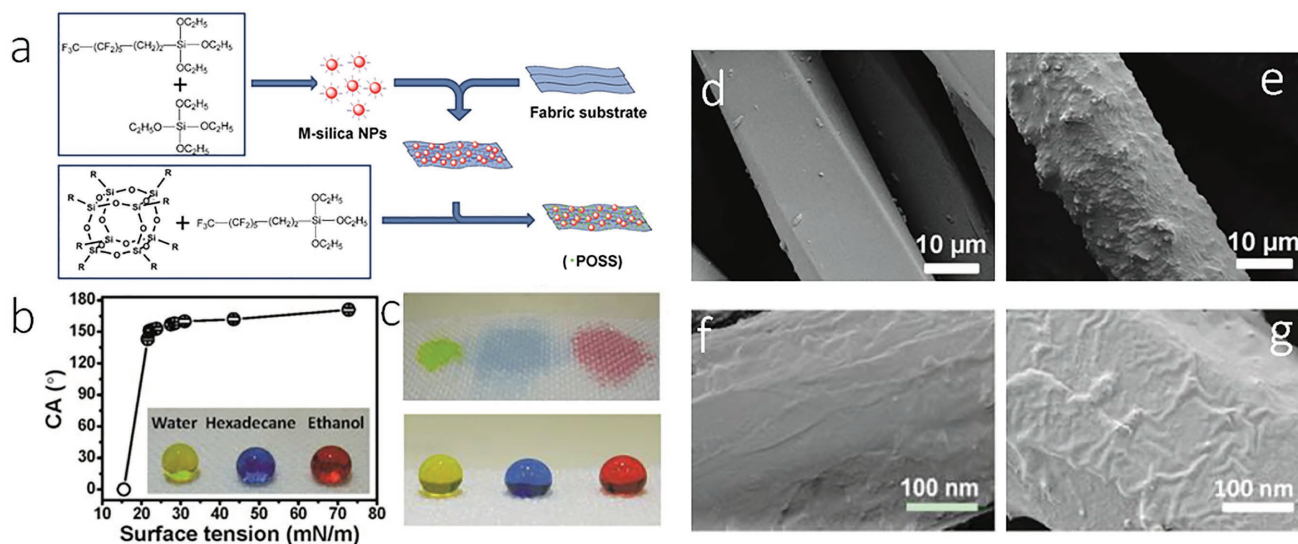


Figure 16. a) Chemical structures of coating materials and procedure for coating treatment, b) the CA change of the coated fabric with surface tension (the insert photo shows water, hexadecane, and ethanol on the coated fabric surface), c) water, hexadecane and ethanol drops on the coated fabric after plasma treatment (top photo) and further heating at 140 °C for 5 min (bottom photo), SEM images of the d) control fiber and e) the superamphiphobic coated fabric, f,g) the coated fabric after 100 cycles of blade scratching, and) further heating at 140 °C for 5 min. Reproduced with permission^[25] Copyright 2013, American Chemical Society.

7. Future Work and Outlook

Despite the fact that considerable progress has been made in the preparation of durable and self-healing SNW fabrics, challenges still remain in the preparation of SNW fabrics in safe, environmentally friendly and low cost manners. In particular, all the superamphiphobic coatings require fluorinated compounds. Some fluorinated chemicals are used which show bio-accumulation and even toxicity. The potential of long chain fluorinated alkyl substances to undergo bioaccumulation in wildlife and to enter the food chain has raised environmental concerns.^[142,143] However, these compounds have been a favored choice to lower surface energy for SNW coatings, especially for preparation of durable and self-healing superamphiphobic fabrics. A search for short-chain fluorinated alkyl substances or fluorine-free chemicals for making superamphiphobic fabrics will be highly desirable.

Although many approaches have been applied to fabricate durable and self-healing SNW fabrics, only a few show feasibility for industrial production due to most of the coating solutions are solvent basis, causing safety issue and pollution to the environment. Thus water-based coatings or physiochemical approaches are highly desired for large-scale production of SNW fabrics.

U-SOP fabrics have been developed by many research groups. However, the durability of the U-SOP fabrics was seldom reported. Little is reported on self-healing U-SOP fabrics either. SHI-SOP fabrics show potential in antipollution and oil-water separation. However, their production is still a challenge. The current drawbacks of SHI-SOP fabrics are the poor oleophobicity and water affinity.

Most developed self-healing SNW surfaces can only heal damage caused by the decomposition of low surface energy materials in the surface layer and superficial abrasions. The fabrication of novel self-healing SNW coatings that can conveniently and repeatedly repair the damaged SNW property caused by severe mechanical damages, such as deep and wide scratches, and abrasions, remains a substantial challenge.

Mobility of low-surface-energy molecules plays an important role in self-healing process, and most of the self-healing were triggered by high temperature heating or long time (at least 12 h) room condition storing, which hinder the practical applications. A very few works reported on NIR light-triggered self-healing and steam ironing triggered healing of superhydrophobic fabric coating. A handy and effective method, such as short time UV (or sunlight) irradiation, rapid healing at ambient conditions etc. needs to be developed to broad their application.

The intrinsic properties of fabrics such as breathability, handle property, and color stability are little considered by researchers during the development of SNW fabrics.

Evaluation of SNW coating durability is very important for textile applications, however, the evaluation methods reported are various. Some of them are lab setup, thus consistent evaluation methods or standards are needed to compare the results from different research groups.

Future efforts are expected to be devoted to developing high-quality durable self-healing SNW fabrics based on nontoxic coating materials, simple coating processes, cost-efficient with mass-production potential, although wet-chemical coating

methods have been widely applied to prepare SNW fabrics. Instead, dry methods are strongly suggested due to their simplicity and no need for organic solvents and any type of additional drying or curing steps. We believe that more versatile and powerful strategies for fabricating durable, self-healing SNW fabrics will be developed from fundamental investigations and practical applications in near future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

durable, fabrics, self-healing, superamphiphobic, superhydrophobic, super-nonwetable, superoleophobic

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