Large-area fabrication of superhydrophobic surfaces for practical applications: an overview

TOPICAL REVIEW

Large-area fabrication of superhydrophobic surfaces for practical applications: an overview

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Abstract
This review summarizes the key topics in the field of large-area fabrication of superhydrophobic surfaces, concentrating on substrates that have been used in commercial applications. Practical approaches to superhydrophobic surface construction and hydrophobization are discussed. Applications of superhydrophobic surfaces are described and future trends in superhydrophobic surfaces are predicted.

1. Introduction

Although surfaces with superhydrophobicity might show different superhydrophobic states [1], those that exhibit apparent contact angles greater than $150°$ with water and low contact angle hysteresis are usually called superhydrophobic surfaces [2]. These surfaces have attracted significant attention within the scientific community over the last two decades because of their unique water-repellent, self-cleaning properties and their potential for practical applications [3–6]. Many strategies to create superhydrophobic surfaces have been put forward [3, 7, 8]. Most of them were inspired by nature [3, 4, 6, 9], and the achieved superhydrophobicity was usually explained by the Cassie–Baxter model [3, 8–10]. In this model, air is trapped in the microgrooves of a rough surface and water droplets rest on a 'composite' surface comprising air and the tops of microprotrusions [5]. The importance of the fractal dimensions of the rough surfaces is well recognized [11, 12] and many approaches have

been based on the fractal contribution. However, regardless of the material (organic or inorganic) used and structure (particles, rod arrays, or pores) formed on the surface, suitable roughness in combination with low surface energy has been required to obtain superhydrophobic surfaces. Until now, procedures of roughening the surface followed by hydrophobization or transforming low-surface-energy materials into rough surfaces have been commonly used to produce superhydrophobic surfaces. Numerous approaches have been attempted, including wax solidification, lithography, vapor deposition, template methods, polymer reconformation, sublimation, plasma, electrospinning, sol–gel processing, electrochemical methods, hydrothermal synthesis, layer-by-layer deposition and one-pot reactions [3]. However, many of the reported preparation techniques of superhydrophobic surfaces involved multistep procedures and harsh conditions, or required specialized reagents and equipment [5]. Many of those methods were expensive and only applicable to small flat surfaces or specific materials [5].

Table 1. Methods of producing superhydrophobic surfaces.

Method	Interactions between substrates and coatings	Roughness formation	Hydrophobization	References
Covalent layer-by-layer assembly	Covalent bonding	Nanoparticle-induced micro/nanostructure	Using low-surface-energy chemicals	[15, 19, 20, 21]
Polymer film roughening	Polymer film itself as substrate or polymer binding	Phase-separation-induced porous structure of a multicomponent mixture	Hydrophobic polymer itself	[5, 13, 23–28]
Chemical vapor deposition	Covalent binding and/or polymer binding	Growth of nanostructures by polymerization	Polymerized structure itself	[34, 35]
Sol–gel process	Covalent binding and/or adhesion	Rough coating	Using low-surface-energy chemicals	[36–38, 41–47]
Hydrothermal synthesis	Covalent binding	Hydrothermal growth of nanostructures	Using low-surface-energy chemicals	[49]
Coating with composites of nanoparticles	Covalent bonding and/or polymer binding	Nanoparticle-induced micro/nanostructure	Using low-surface-energy chemicals or hydrophobic polymers	[42, 50]

Also, many approaches did not focus on the durability and robustness of the superhydrophobicity and of the obtained materials. Consequently, very few products were launched realizing practical applications of such functional materials.

Numerous research articles reported fabrication of superhydrophobic surfaces within the past few years. There were also several reviews on the theory and applications of superhydrophobic surfaces [3, 4, 8, 9, 13, 14]. This review focuses on recent research on the fabrication of superhydrophobic materials for current, rather than potential applications.

2. Substrates for superhydrophobic surfaces

2.1. Rigid surfaces

Fundamental research on superhydrophobic surfaces was mostly conducted on such rigid solid substrates as silicon wafers, glass slides and metal surfaces. These substrates might limit the practical applications as well as the large-scale production of superhydrophobic surfaces [15]. However, it should be noted that practical applications depend not only on the substrates but also on the feasibility of the treatment techniques.

2.2. Flexible surfaces

Superhydrophobic surfaces on flexible substrates should be preferable to those on rigid substrates for industrial applications. One example of flexible substrates is polymer films with rough surfaces and low surface energy. Their rough surfaces can be cast, spray coated or post treated. The low surface energy might be intrinsic to the polymeric material or imparted by hydrophobization.

Another example of flexible surfaces is fibrous substrates, most of which are woven or nonwoven textiles with natural or synthetic microfibers. Superhydrophobic surfaces on textiles have recently received much interest owing to their simple fabrication, the availability of raw materials, their potential large-scale production [16] by industrial techniques [15, 17],

and their practical applications in many areas. For instance, the waterproofing of textiles is one of the primary areas with a long history [18]. Textiles with a superhydrophobic coating could find applications as water-resistant apparel and would generally be useful for any application in which textile surfaces are exposed to the environment.

3. Practical approaches to realizing superhydrophobic surfaces

The criteria for practical application in this review mainly include the following two considerations. One is the durability and robustness of the surface and its superhydrophobicity. The other is the feasibility of the scale-up production devoid of harsh conditions. This review focuses on the approaches of covalent layer-by-layer assembly, polymer film roughening, chemical vapor deposition, sol–gel processing, hydrothermal synthesis and coating with nanoparticle composites. The main approaches to realizing superhydrophobic surfaces are summarized in table 1. Some studies might not be cited in this review for brevity; this does not indicate any judgment of the omitted studies.

3.1. Covalent layer-by-layer assembly

Layer-by-layer assembly is a versatile way to construct thin-film nanocomposites and to modify surfaces. This technology is popular because it is simple and forgiving [19]. It is most commonly used to fabricate an interface involving a multilayer ionic assembly of polyelectrolytes. However, some ionic assemblies are of limited applicability because of the weak interaction between the substrate and the layers. This review focuses on layer-by-layer assembly approaches that use covalent bonds to form multilayer grafts, which are durable, stable and practical.

As shown in figure 1, the design of chemical reactions between layers is very important since it affects the stability of the formed coating as well as the feasibility of the process. Usually, functionalized nanoparticles facilitate the production
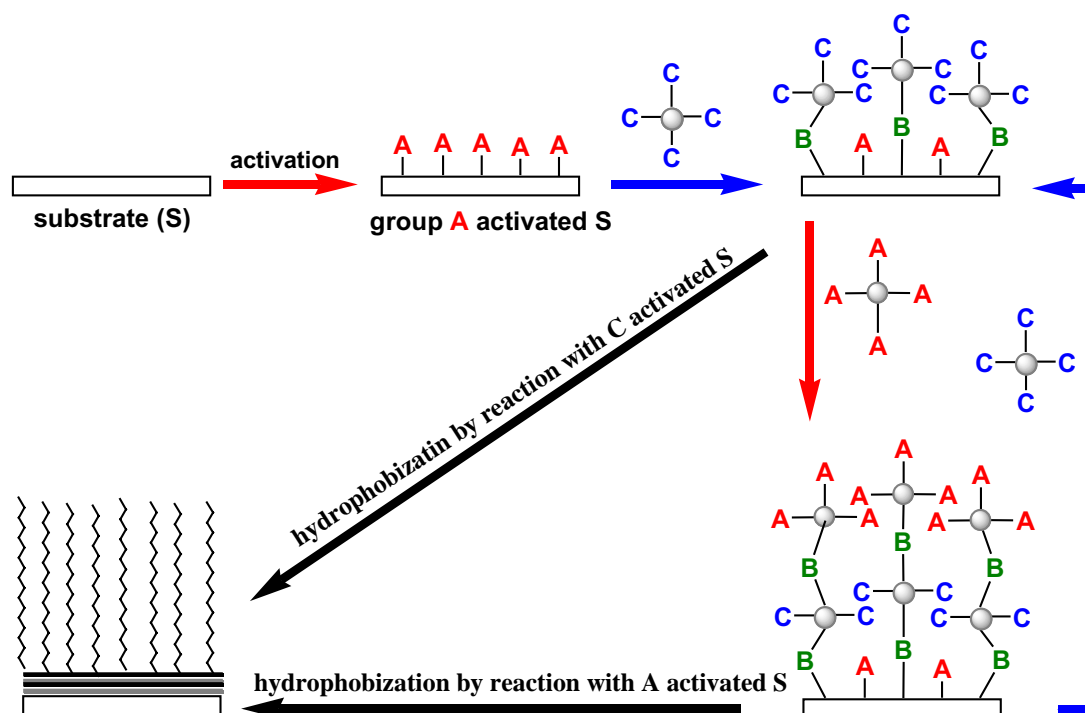
Figure 1. Steps used in the covalent layer-by-layer assembly of functional particles, with C groups and A groups on a substrate activated with A groups, for superhydrophobic surfaces. B groups are formed by the reactions of A groups with C groups.

of rough surfaces on a substrate simply by controlling the nanoparticle layers. To enhance the interaction between the first layer and the substrate, the substrate should usually be activated. After layer-by-layer assembly, the outer surface usually contains residual functional groups, marked by letters A and C in figure 1, which can be utilized to react with low-surface-energy agents for covalent hydrophobization.

As shown in figure 2, Ming *et al* [20] reported a simple and robust procedure for preparing superhydrophobic films with a dual-size hierarchical structure originating from well-defined raspberry-like particles. Firstly, a conventional cross-linked film based on an epoxy–amine system was prepared with unreacted epoxy groups available for further surface grafting. Secondly, raspberry-like silica particles with an amine-functionalized surface were chemically deposited onto the epoxy films, generating roughness with two characteristic length scales. Finally, a layer of monoepoxy-end-capped poly(dimethylsiloxane) was grafted onto the raspberry-like particles to render the film surface hydrophobic. Adopting a similar concept, Amigoni *et al* [21] constructed hybrid organic/inorganic surfaces by alternating different layers of amino-functionalized silica nanoparticles and epoxy-functionalized silica nanoparticles. Then, hydrophobization of the last layer of amino-functionalized silica particles was carried out by grafting a newly designed, highly fluorinated aldehyde, creating a monomolecular layer via the formation of an imine. The hydrophobicity increased with the number of layers, and stable, highly superhydrophobic surfaces were obtained.

As shown in figure 3, we [15, 16] prepared super-hydrophobic surfaces on cotton textiles by a complex coating

of amino- and epoxy-functionalized silica nanoparticles on epoxy-functionalized cotton textiles to generate a dual-size surface roughness, followed by hydrophobization with stearic acid, $1H,1H,2H,2H$-perfluorodecyltrichlorosilane, or their combination. The epoxy-functionalization of the cotton enhanced the interaction between the fiber and the silica coating. The incorporation of the functionalized SiO_2 particles not only generated a firm dual-size rough surface but also facilitated its further hydrophobization. The produced coatings were robust and exhibited stable superhydrophobicity.

Manca *et al* [22] presented a robust and cost-effective coating method to fabricate surfaces with durable superhydrophobic and antireflective properties. They used a sol–gel process to produce a double-layer coating comprising silica nanoparticles with a trimethylsiloxane-functionalized surface which were partially embedded into an organosilica binder matrix. A dense and homogeneous organosilica gel layer was first coated onto a glass substrate, and then a trimethylsilanized nanosphere-based superhydrophobic layer was deposited onto it. After thermal curing, the two layers merged into a monolithic film, and the hydrophobic nanoparticles were permanently attached to the glass substrate. Such treated surfaces exhibited superhydrophobicity with a contact angle of $168°$ and a stable self-cleaning effect during $2000\,h$ of outdoor exposure.

3.2. Polymer film roughening

Because of their film-forming property and flexibility, polymers are of interest for the fabrication of superhydrophobic surfaces. Polymer-based rough surfaces
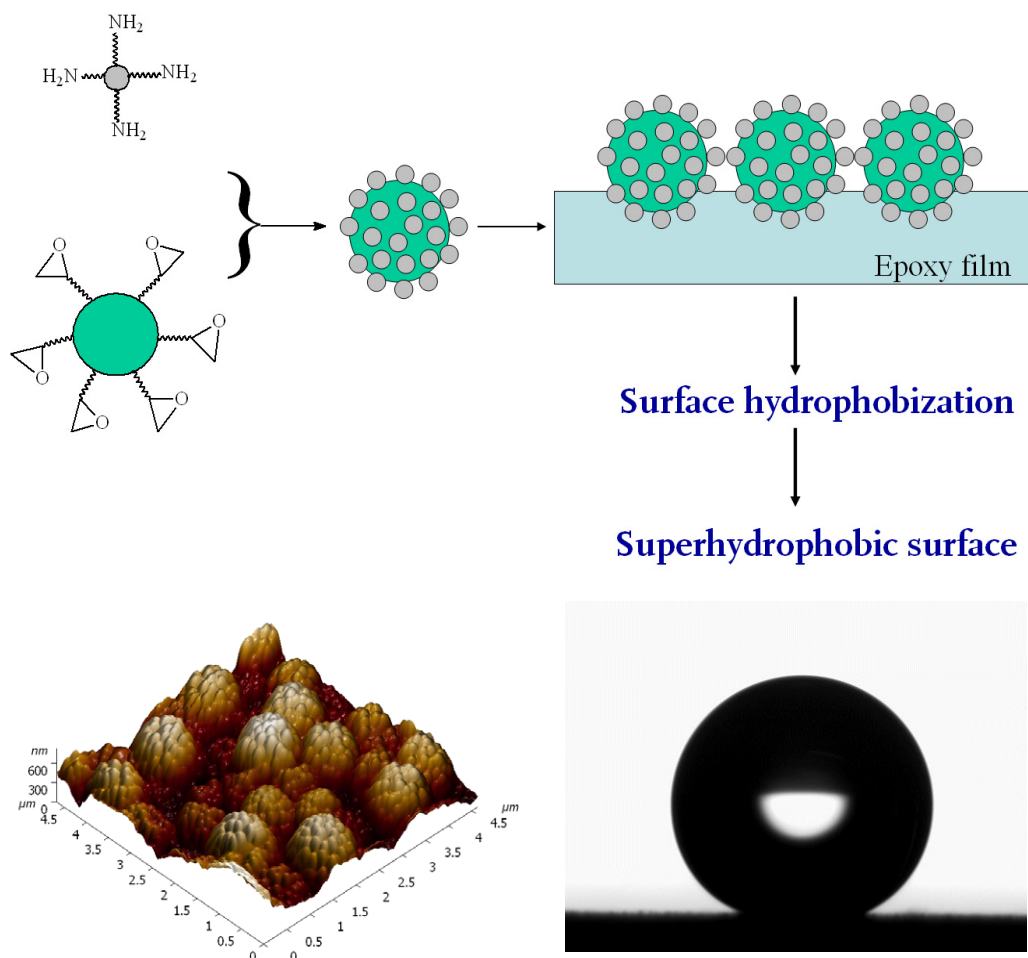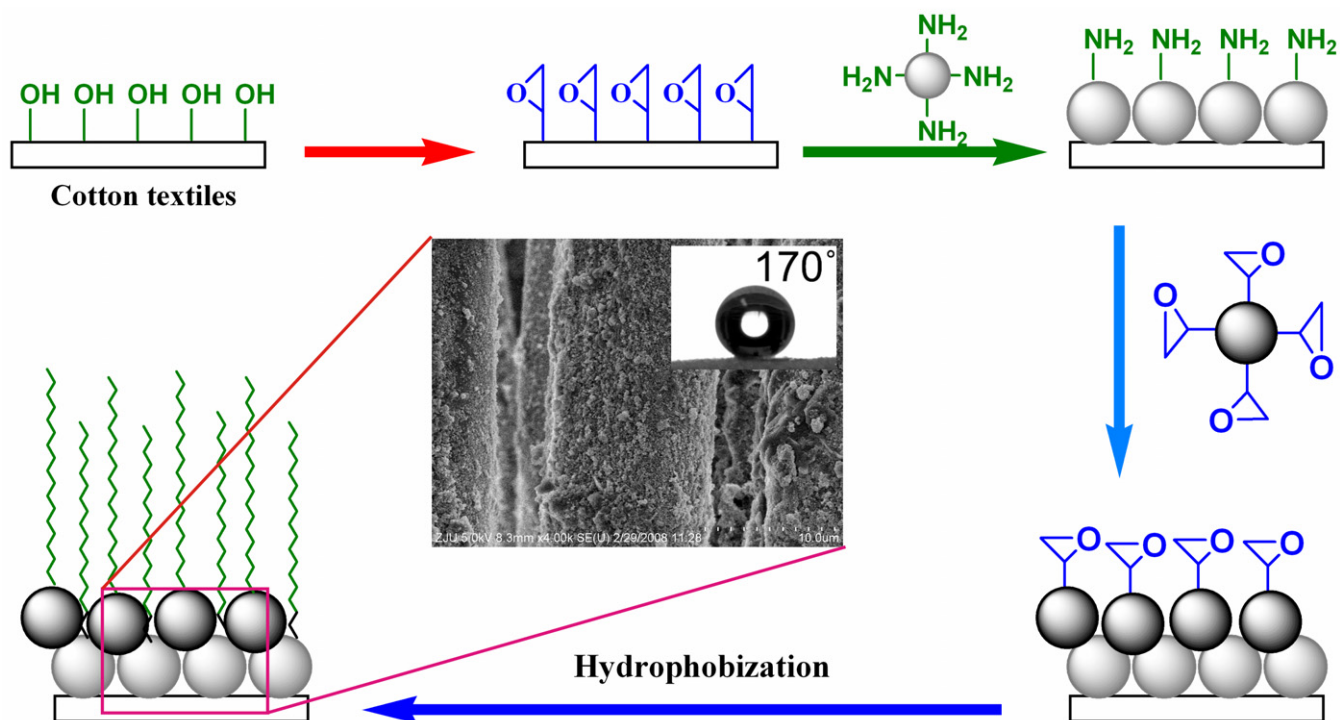
Figure 2. Preparation of superhydrophobic films based on covalent assembly yielding raspberry-like particles (reprinted with permission from [20], © 2005 American Chemical Society).

can be formed by the phase separation of a multicomponent mixture [13]. If a stable mixture becomes unstable owing to changes such as cooling or solvent evaporation, it will begin to separate into two phases, one of which might be a solid or become solid at some point in the process. This creates a solid porous structure, as shown in figure 4(a), or a lotus-like structure with micro- and nanopapillae, as shown in figure 4(b). The size of the pores or papillae in the formed solid structures can be controlled if the rate of phase separation can be altered relative to the rate of solidification. Phase separation has received great interest for the fabrication of superhydrophobic surfaces owing to its low cost, ease of production and the possibility of creating substrates with various shapes by casting and coating.

Franco *et al* [23] fabricated a superhydrophobic polypropylene membrane by a solvent casting of polypropylene and utilizing the surface roughness and porosity developed with a nonsolvent, as shown in figure 4(a). The chemical treatment increased the contact angle of polypropylene by 42° and that of polytetrafluoroethylene by 30°. Lu *et al* [24] fabricated a low-density polyethylene superhydrophobic surface by controlling its crystallization

behavior in a stress field to produce a gel-like porous coating. The contact angle with water reached 173° on various substrates. Yuan *et al* [25] reported the preparation of a stable superhydrophobic high-density polyethylene surface by adding ethanol in a humid atmosphere at 5 °C.

Levkin *et al* [5] reported a facile and inexpensive approach to the formation of superhydrophobic polymer coatings. Their method involved the *in situ* polymerization of common monomers (butyl methacrylate, ethylene dimethacrylate, 2-hydroxyethyl methacrylate, styrene and 1,4-divinylbenzene) in the presence of a porogenic solvent (1-decanol, cyclohexanol and/or tetrahydrofuran), which resulted in phase separation and production of superhydrophobic surfaces with the desired combination of micro- and nanoscale roughness. The method was applicable to a variety of substrates and was not limited to small areas or flat surfaces. The polymerized material could be ground into a superhydrophobic powder, which, once applied to a surface, rendered it superhydrophobic. The morphology of the porous polymer structure could be efficiently controlled by the composition of the polymerization mixture, whereas the surface chemistry could be adjusted by photografting.

Figure 3. Preparation of superhydrophobic surfaces on cotton textiles by complex coating of silica nanoparticles and hydrophobization (reprinted with permission from [15], © 2009 Elsevier B.V.).
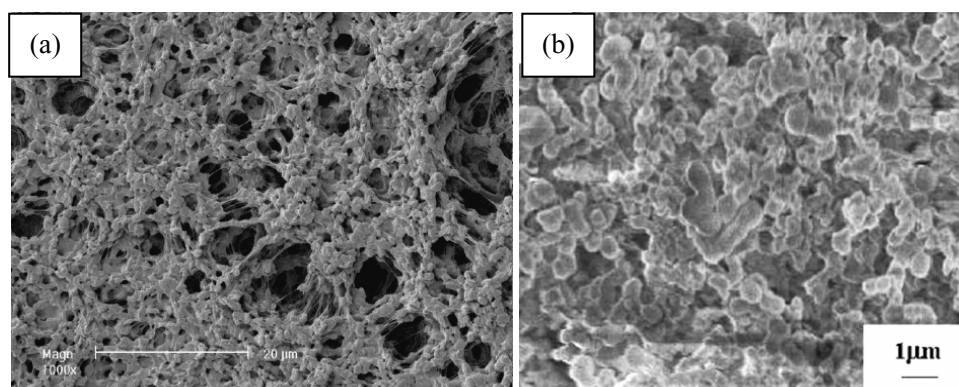
Figure 4. SEM images of (a) porous membrane produced by solvent casting of 17.9 mg ml^{-1} polypropylene solution using methyl ethyl ketone as the nonsolvent (reprinted with permission from [23], © 2008 Elsevier B.V.); (b) superhydrophobic poly(vinyl chloride) film obtained by coating with a mixture of 2 : 1 (v/v) ethanol and H$_2$O as the nonsolvent (reprinted with permission from [27], © 2006 Elsevier B.V.).

Morphology control was used to reduce the globule size of the porous architecture from micro- to nanoscale, thereby producing a transparent material.

Zhang *et al* [26] described a simple and economical method of obtaining a superhydrophobic surface on a wool textile with a comb-like polymer comprising acrylate and organic siloxane. The combination of acrylate and organic siloxane resulted in unique characteristics. Firstly, the acrylate polymer chains could contribute to the increase in cohesiveness and film-forming properties. Secondly, the long Si–O–Si chains, characterized by a low surface energy, could be utilized to enhance the water repellency. In addition, the Si–O–Si chains could migrate toward the surface of the outer

layers, resulting in the formation of a surface with nanoscale roughness. To achieve this goal, poly(acrylate-g-siloxane) was prepared by emulsion copolymerization of acrylate with silicone oligomers containing a double bond. After being treated with the resulting emulsion, the wool textile exhibited excellent superhydrophobicity.

Superhydrophobic poly(vinyl chloride) [27, 28] and polycarbonate [29] coatings were also fabricated on the basis of the roughness induced by a nonsolvent.

Another method of producing rough polymer films uses incorporation of inorganic nanoparticles, in which the polymer acts as a binder with low surface energy. Thus, durable superhydrophobic surfaces can be
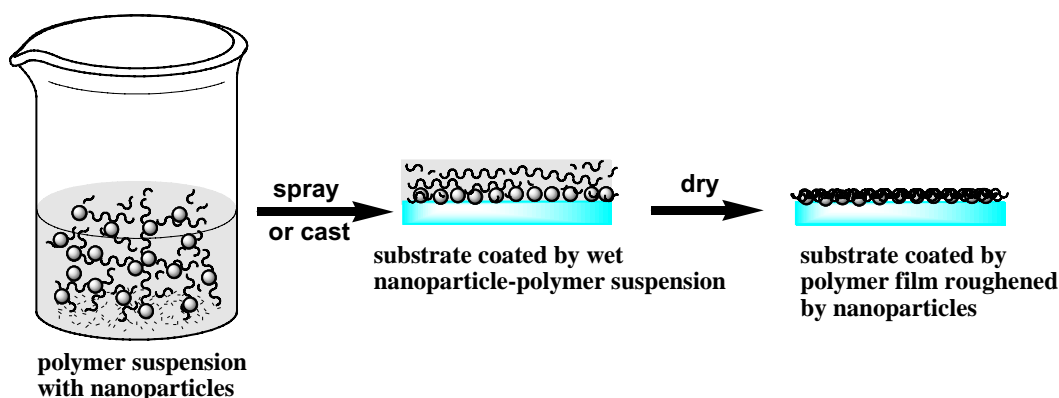
Figure 5. Nanoparticle-polymer composite coating for superhydrophobic surfaces.
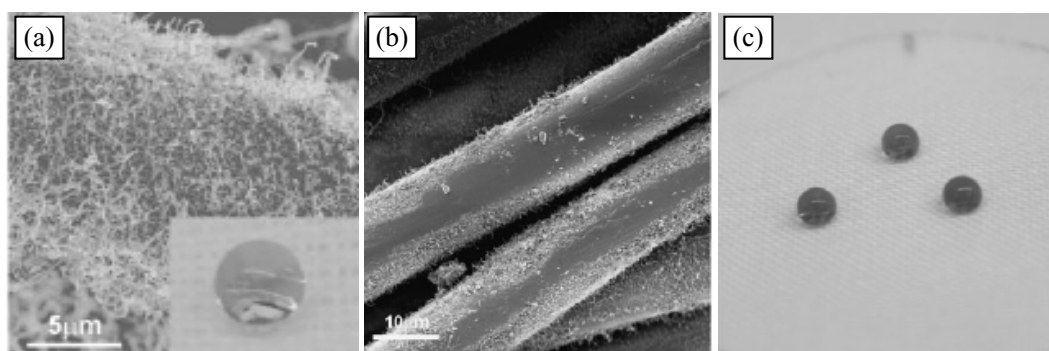

Figure 6. SEM images of (a) poly(ethylene terephthalate) textile fabric coated with silicone nanofilaments and (b) coated samples after the abrasion test (Textile Friction Analyzer, 1450 cycles, load: 5 N, corresponding to a contact pressure of 7.8 kPa) and (c) drops of water showing the wetting properties of the sample after the abrasion test. The inset of the SEM image in (a) shows a drop of water deposited on the coated fabric (reprinted with permission from [34], © 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

obtained even without post-hydrophobization, as shown in figure 5. Steele *et al* [30] described a technique for fabricating superoleophobic coatings by spray-casting nanoparticle-polymer suspensions. The method used ZnO nanoparticles blended with a waterborne perfluoroacrylic polymer emulsion and cosolvents to produce self-assembling nanocomposite slurries that form a hierarchical nanotextured morphology upon curing. The resulting surface attained high contact angles and low contact angle hysteresis. The coatings could be easily applied to large and/or flexible substrates by spray coating and required no additional surface treatment by commonly used hydrophobic molecules such as fluorosilanes. Cao *et al* [31] used composites based on organosilane-modified silica nanoparticles and an acrylic polymer binder to fabricate superhydrophobic surfaces with anti-icing capability. Utilizing the polymer binder, their composites could be coated on a variety of substrates. They applied the composites to aluminum plates using a spray gun and cured them at room temperature for 12 h. The obtained surfaces could prevent ice formation upon impact of supercooled water either under laboratory conditions or in natural environments. Manoudis *et al* [32, 33] fabricated superhydrophobic surfaces for the enhanced protection of stone by adding silica nanoparticles into a commercial siloxane composition, thereby enhancing its protective efficiency. The extent of surface hydrophobization depended

on the nanoparticle concentration and reached a maximum value of ∼160° at 1% w/v of nanoparticles for white Greek marble treated with the modified composition.

3.3. Chemical vapor deposition

Chemical vapor deposition is a technique whereby gaseous reactants can be deposited onto a substrate to form a nonvolatile solid film. The film morphology is mostly dependent on the surface morphology of the substrate, which is usually used as a template. However, through selection of the gaseous reactants and adjustment of the reaction conditions, different morphologies can be realized on the substrate.

As shown in figure 6, Zimmermann *et al* [34] prepared superhydrophobic textile fabrics via a one-step gas phase coating procedure by growing a layer of polymethylsilsesquioxane nanofilaments onto individual textile fibers. Eleven textile fabrics made from natural and synthetic fibers were successfully coated and their superhydrophobic properties were evaluated. A thorough investigation of the commercially relevant poly(ethylene terephthalate) fabric revealed an unparalleled long-term water resistance and stability of the superhydrophobic effect. Because of the special surface geometry generated by the nanoscopic, fibrous coating on the microscopic,
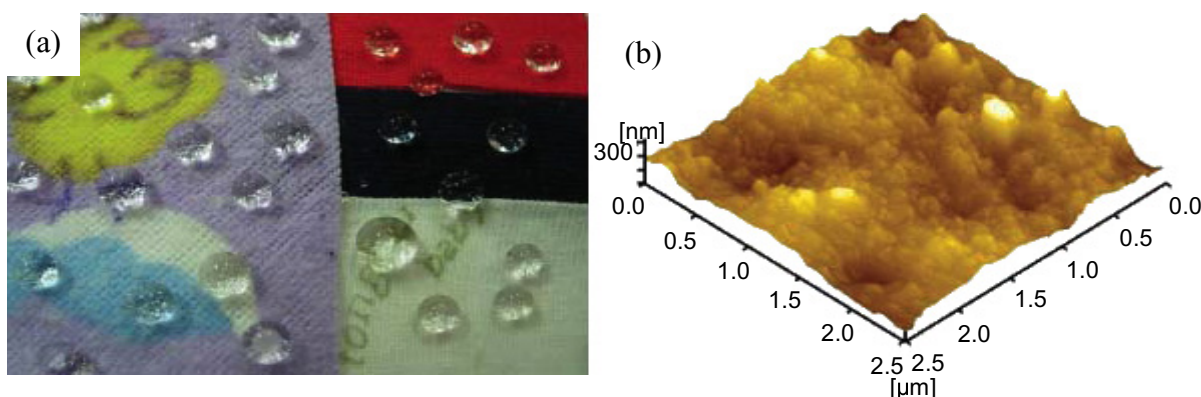
Figure 7. Water droplets on the surface of a modified colored cotton fabric (a) and 3D atomic force microscopy image of the modified fiber surface (b) (reprinted with permission from [35], © 2007 Royal Society of Chemistry).

fibrous textiles, the coated fabric remained completely dry even after two months of immersion in water and remained superhydrophobic even after continuous rubbing with a skin-simulating material under a significant load. Furthermore, important textile parameters such as tensile strength, color and haptics were unaffected by the silicone nanofilament coating.

Li *et al* [35] transformed hydrophilic cellulose into superhydrophobic cellulose via chemical vapor deposition followed by hydrolyzation and polymerization. First, a sheet of cotton fabric was ultrasonically cleaned in ethanol and in water and dried. Then it was placed in a sealed chamber and exposed to a saturated atmosphere of trichloromethylsilane. Next, the fabric was immersed at room temperature into an aqueous solution of pyridine to hydrolyze the remaining Si–Cl bonds. The fabric was carefully washed with water to remove the excess reagents. Finally, it was treated in an oven at $150\,^{\circ}C$ for 10 min. Subsequent polymerization of the Si–OH groups resulted in a nanoscale silicone coating tightly attached to the surface with no changes in morphology and color of the original cotton fabric, as shown in figure 7.

3.4. Sol–gel process

Sol–gel processing is a well-recognized method of synthesizing gels and nanoparticles. Sol–gel research has resulted in technologies enabling the production of multilayered films, porous pillars, thin films, nanocrystalline materials, nanopowders, rough coatings and clusters for paints, antiseptics, nanocomposites, drugs, biomedical implants and military components. The surface roughness obtained with the sol–gel method can be easily tuned by changing the protocol of the method and the composition of the reaction mixture.

Silica coating based on tetramethoxysilane or tetraethyoxysilane is widely adopted for the sol–gel method. Xiu *et al* [36] incorporated isobutyltrimethoxysilane into silica layers, which produced hydrophobic isobutyl surface groups and generated surface hydrophobicity. Taurino *et al* [37] selected commercial metal alkoxides, tetraethoxysilane, tetraethyl orthotitanate and tetra-n-propyl zirconate as precursors, taking their different reactivities

into account. They utilized α,ω-triethoxysilane-terminated perfluoropolyether as a low-surface-energy material to prepare superhydrophobic coatings via a sol–gel process. Different reactivities of the precursors resulted in different surface morphologies and surface free energies due to the demixing of the forming phases. This method can be applied to a variety of substrates, such as silicon wafers, glasses, metals and polymer surfaces, with little or no surface pretreatment.

Latthe *et al* [38] described the synthesis of superhydrophobic silica films on glass substrates using trimethylethoxysilane as a co-precursor. The coating sol was prepared by keeping the molar ratio of tetraethoxysilane precursor, methanol and water at 1:38.6:8.68, using 2 M NH_4OH throughout the experiments, and the molar ratio (M) of trimethylethoxysilane to tetraethoxysilane was varied from 0 to 1.1. The hydrophobicity of the films increased with increasing M value; however, the optical transmission decreased from 88 to 82% in the visible range. Silica films with a static water contact angle as high as $151°$ and a sliding angle of $8°$ have been produced from a sol with an M value of 1.1. The hydrophobic silica films retained their hydrophobicity up to $275\,^{\circ}C$. These films were transparent and stable to high temperature and humidity. By modifying silica sols with trimethylethoxysilane, sol–gel coatings could be prepared on glass substrates at room temperature. The coatings had excellent water-repelling properties without any addition of fluorine-containing compounds.

Gan *et al* [39] fabricated highly hydrophobic surfaces on cotton and polyester fabrics using a silica sol–gel coating and treatment with hydrolyzed hexadecyltrimethoxysilane. The processed textile fabrics showed excellent water repellency with water contact angles as high as $155°$ on cotton and $143°$ on polyester.

Daoud *et al* [40] prepared transparent and durable superhydrophobic surfaces on knit and woven cotton substrates using a modified silica sol, which was produced via cohydrolysis and polycondensation of a mixture of hexadecyltrimethoxysilane, tetraethoxyorthosilcate and 3-glycidoxypropyltrimethoxysilane. By comparing the contact angle and water gain values before and after washing, they showed that the hydrophobic property
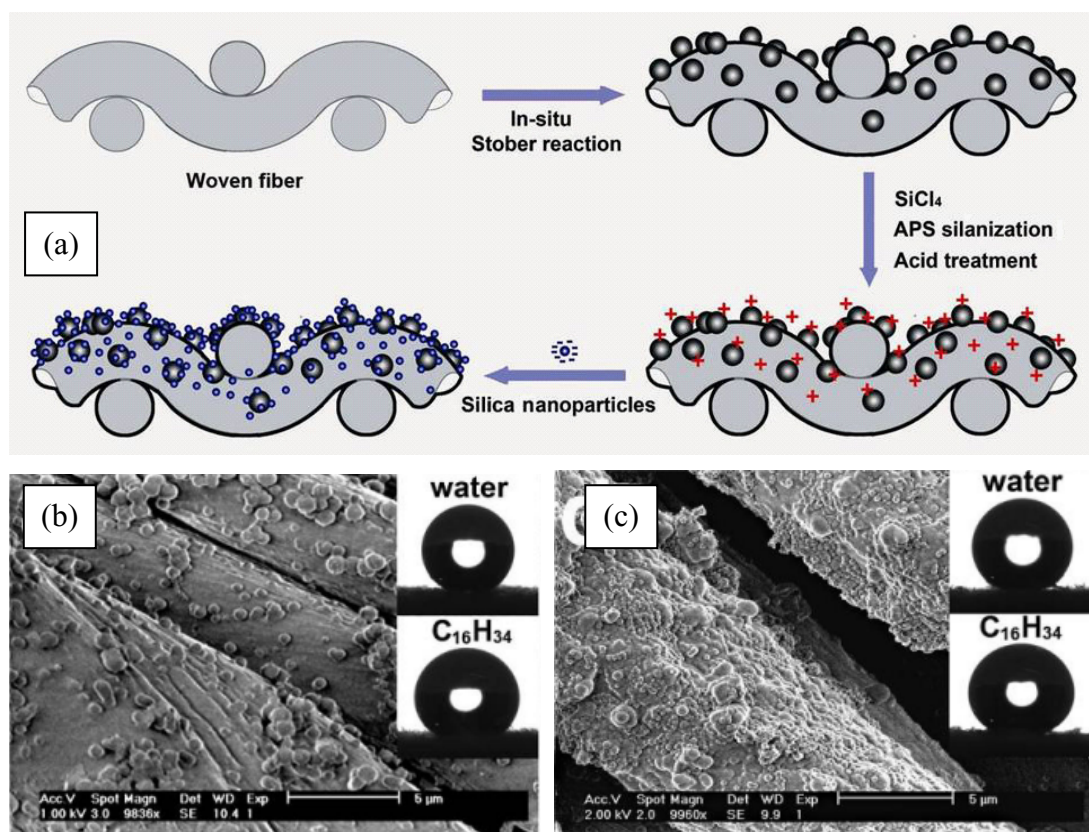
Figure 8. (a) Schematic illustration of the procedure for the preparation of dual-size structure on the surface of woven cotton fibers, combining an *in situ* Stöber reaction with the subsequent adsorption of silica nanoparticles, and morphology of samples obtained by (b) *in situ* introduction of silica microparticles on cotton fibers and (c) three-cycle adsorption of silica nanoparticles on sample (a) (reprinted with permission from [42], © 2009 American Chemical Society).

was still present even after ten cycles of washing. This stability was attributed to the linking properties of 3-glycidoxypropyltrimethoxysilane, which promoted strong adhesion to the cotton substrates.

Hoefnagels *et al* [41] reported the fabrication of biomimetic superhydrophobic cotton textiles by either a one-step or two-step reaction. They synthesized silica particles coated with amine groups *in situ*, which were covalently bonded to the cotton fibers; the amine groups were then utilized to hydrophobize the surface via the reaction with mono-epoxy-functionalized polydimethylsiloxane. When $1H,1H,2H,2H$-perfluorodecyl trichlorosilane was used for the surface modification, oleophobic textiles were obtained with a static contact angle of $140°$ and a roll-off angle of $24°$ for a $15\,\mu$l sunflower oil droplet. Later, Leng *et al* [42] described the preparation of superoleophobic cotton textiles based on a structure having multiple length scales. The produced surface had a high hexadecane contact angle ($153°$ for $5\,\mu$l droplets) as shown in figures 8(b) and (c), and a low roll-off angle ($9°$ for $20\,\mu$l droplets). The multiple length scales of the roughness originated from the woven structure having two additional layers of silica particles (microparticles and nanoparticles), which were covalently bonded to the fiber as schematically shown in figure 8(a).

We [43] prepared superhydrophobic cotton fabrics by sol–gel coating of TiO$_2$ and surface hydrophobization. The

superhydrophobicity of the resulting fabrics depended on the roughness caused by the sol–gel coating rather than the concentration of TiO$_2$.

Yu *et al* [44] prepared a silica sol with an appropriate particle size and synthesized a perfluorooctylated quaternary ammonium silane coupling agent. The silica sol and coupling agent were applied to cotton fabrics by a conventional pad-dry-cure process. The fabrics treated with both silica sol and the silane coupling agent exhibited high hydrophobicity and oleophobicity.

Li *et al* [45] used sodium silicate, a cheap and commonly used industrial raw material, as the precursor to prepare a silica sol by acid-catalyzed hydrolysis and condensation. After dip-coating the silica sol onto cotton surfaces, the surfaces were modified with hexadecyltrimethoxysilane to obtain a thin layer through self-assembly. The treated cotton fabrics exhibited superhydrophobicity.

Bae *et al* [46] have imparted superhydrophobicity to a hydrophilic cotton fabric by a combined treatment with silica nanoparticles and a cost-effective commercial water-repellent agent. For cotton fabrics treated with silica nanoparticles with an average diameter of $378\,$nm, water contact angles above $130°$ were easily obtained even with a very low water-repellent agent concentration of $0.1\,$wt%. The cotton fabric treated with only the water-repellent agent was not hydrophobic.
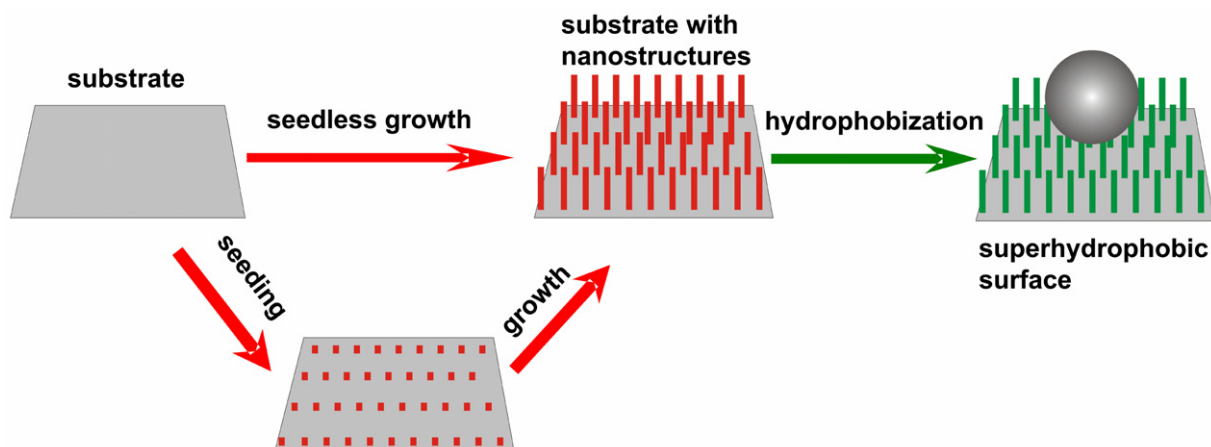
Figure 9. Fabrication of superhydrophobic surfaces by hydrothermal growth of nanostructured surface and hydrophobization.

Wang *et al* [47] have produced stable superhydrophobic surfaces with water contact angles over 170° and sliding angles below 7° by simply coating a particulate silica sol solution of cohydrolyzed tetraethoxysilane/fluorinated alkyl silane with $NH_3 \cdot H_2O$ on various substrates, including textile fabrics (e.g. polyester, wool and cotton) and electrospun nanofiber mats.

It should be mentioned that the superhydrophobic coatings obtained through the sol–gel treatment of substrates with hydroxyl groups might be stable owing to the formation of covalent bonds between the coating and substrate by condensation in the sol–gel process or/and dehydration in the curing process; these processes result in a robust coating.

3.5. Hydrothermal synthesis

Hydrothermal synthesis is a well-known method for the fabrication of nano/microscale materials. There has been considerable research on the growth of ZnO materials with different structures on substrates to fabricate superhydrophobic surfaces. As shown in figure 9, this method usually includes two steps. First, ZnO micro/nanostructures are grown in a basic solution of Zn^{2+} on the target substrate, which might have been pretreated by ZnO seeding. Then the as-prepared rough surface is hydrophobized by a layer of polymers or small molecules to obtain a superhydrophobic surface. This wet chemical route could be applied to a variety of substrates, such as silicon wafers, glasses and even polymer surfaces, regardless of their irregular shapes or curved surfaces. This advantage makes this process favorable for practical applications such as aircrafts, ships and some special decorations [48].

Xu and Cai [49] employed a hydrothermal method to create superhydrophobic surfaces on cotton fabrics. Firstly, ZnO nanocrystals were prepared and applied to cotton fibers. Then, oriented ZnO nanorod arrays were fabricated on the fibers to form nanoscale roughness. Finally, the as-obtained fabrics were modified by dodecyltrimethoxysilane to obtain superhydrophobic surfaces. This method showed very good reproducibility and involved inexpensive laboratory equipment used for conventional textile processing. Two

factors were associated with the enhanced attachment between the cotton fiber substrate and the ZnO nanorods, as shown in figure 10. Dodecyltrimethoxysilane was infiltrated above and below the ZnO seed layer as a binding agent when the cotton fabric was immersed in an ethanolic solution of dodecyltrimethoxysilane. The Si–OH groups in the hydrolyzed dodecyltrimethoxysilane reacted with both the ZnO seeds and the cotton fiber substrate, since there were abundant hydroxyl groups on the ZnO seeds and cotton fiber surface. Consequently, the ZnO seeds and the fiber substrate were tightly bound to each other. Furthermore, there were three hydroxyl groups in each hydrolyzed dodecyltrimethoxysilane molecule, and hydrolyzed dodecyltrimethoxysilane could easily form cross-linked chains. Thus, the nanorods were firmly bundled and fixed on the ZnO seeding layer. The two layers created in this process successfully improved the adhesion and stability of the ZnO nanorods on the cotton substrate.

3.6. Coating with composites of nanoparticles

Well-defined coating of nano/microparticles on fibers is a promising way to produce rough surfaces on textiles. To improve the coating rate and the durability of superhydrophobicity, particles or/and textile substrates are usually modified by introduction of functional groups, such as carboxyl, amino, epoxy and hydroxyl groups. In this way, the particles can covalently react with each other and with the textile fibers to form a firm coating. The remaining functional groups on the coating surface can then facilitate further hydrophobization with low-surface-energy materials.

Ramaratnam *et al* [50] prepared ultrahydrophobic textile surfaces through the decoration of fibers with a monolayer of reactive nanoparticles and a nonfluorinated polymer. In the first step of surface modification, silica particles covered with an ultrathin reactive layer of poly(glycidyl methacrylate), an epoxy-containing polymer, were deposited on a fiber surface. The silica particles covered with epoxy functional groups are capable of reacting with a fiber surface containing complementary (e.g. carboxy and hydroxy) functional groups and with hydrophobic polymers possessing functional groups
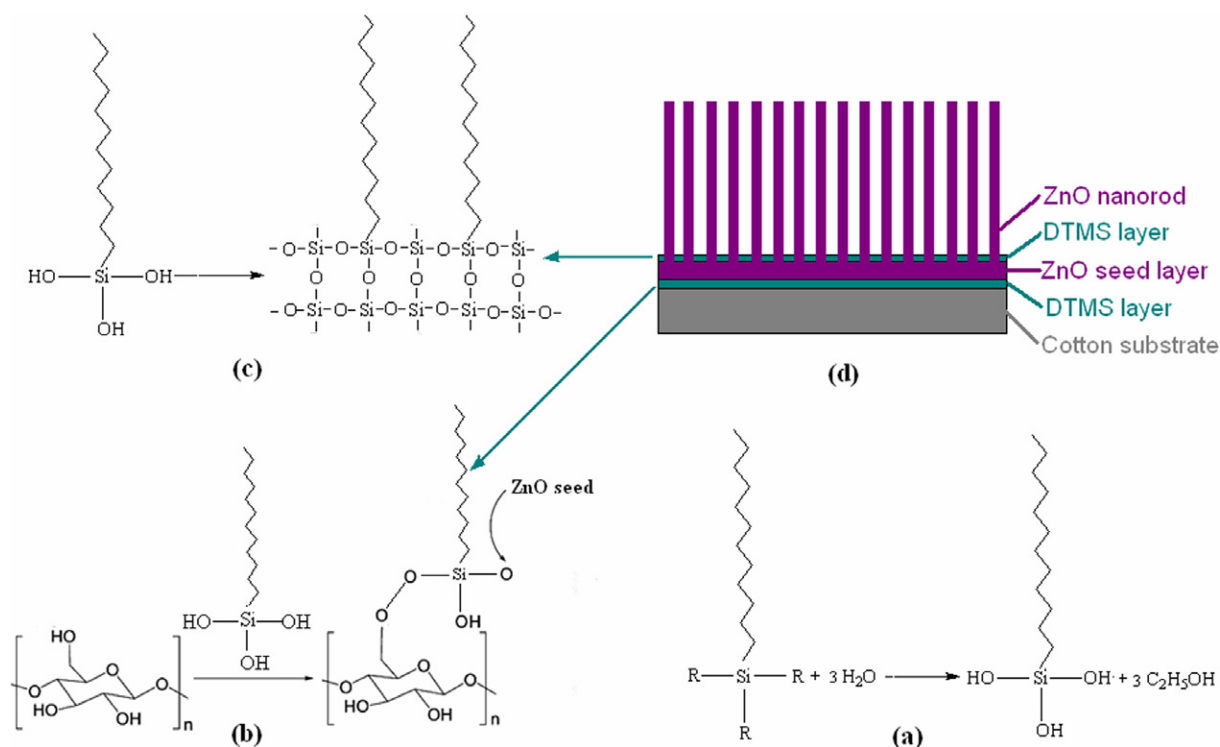
Figure 10. Scheme showing the structure of dodecyltrimethoxysilane-treated fiber for improved adhesion and stability of ZnO nanorods to a cotton substrate (reprinted with permission from [49], © 2008 Elsevier B.V.).

that exhibit affinity for the epoxy modified surface. During the second step, a hydrophobic polymer was grafted to the surface of the fibers and nanoparticles, and an ultrathin rough hydrophobic layer was generated, which was chemically anchored to the fiber boundary.

Leng *et al* [42] introduced raspberry-like, dual-size structures onto woven cotton fibers, thereby producing a surface structure with three characteristic length scales (figure 8). Relatively large silica particles were generated *in situ* and covalently bonded to the cotton fibers. After treatment with 3-aminopropyl-triethoxysiloxane and hydrochloric acid, the surface charge became positive due to the protonation of amine groups. Negatively charged silica nanoparticles were then electrostatically attached to the fiber surface. The obtained roughened structure was stabilized by $SiCl_4$ cross-linking, followed by surface modification with $1H,1H,2H,2H$-perfluorodecyl trichlorosilane. The modified textiles were completely nonwettable by water and hexadecane, with both liquids showing high contact and low roll-off angles.

4. Hydrophobization

After the coating has been roughened, most substrates still do not exhibit superhydrophobicity. It is necessary to lower the surface energy of the roughened surfaces. Previously, various low-surface-energy coatings have been developed to modify organic and inorganic rough surfaces and induce superhydrophobicity. The commonly used reactive molecules for low-surface-energy modification are shown in figure 11, which are mainly long alkyl chain thiols, alkyl or
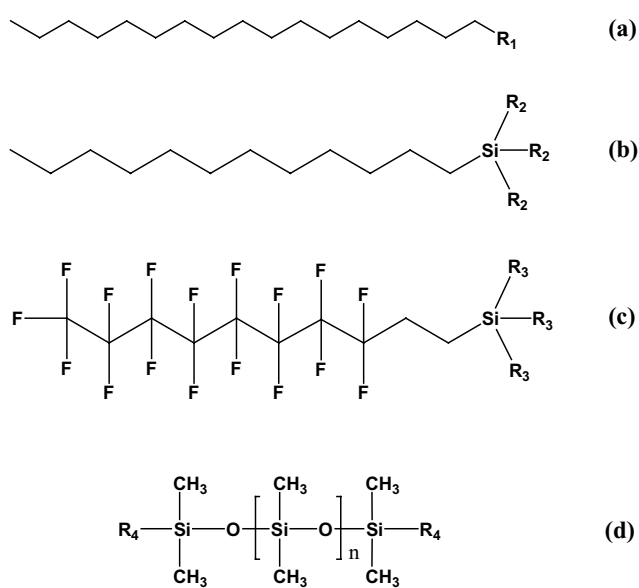
Figure 11. Examples of surface reactive molecules for low-surface-energy modification: (a) long alkyl chain with R_1 groups; (b) long alkyl chain organic silanes with R_2 groups; (c) long alkyl chain fluorinated silanes with R_3 groups, in which R_1 can be –SH, –OH, –COOH, –NH_2, etc, and R_2 and R_3 can be –Cl, –OCH_3, –OCH_2CH_3; the length of these chains can be varied from C8 to C18; and (d) polymers based on polydimethylsiloxane, which can be bis-end-capped or mono-end-capped, where R_4 is usually a 3-aminopropyl or glycidyl ether group.

fluorinated organic silanes, perfluorinated alkyl agents, long alkyl chain fatty acids, polydimethylsiloxane-based polymers or other polymers, or their combinations. Among others,

commercially available products such as water repellents and poly(acrylate-g-siloxane) textile finishing agent can also be used.

4.1. Hydrophobization with fluorinated molecules

The most commonly used chemicals for hydrophobization are fluoroalkylsilanes owing to their extremely low surface free energy and the simple reaction of the silane groups with the hydroxyl groups on coatings [41, 42, 44]. Also, most superoleophobic surfaces are created by the hydrophobization of a perfluorinated material [41, 42].

4.2. Hydrophobization with alkyl molecules

Fluorochemicals have extremely low surface free energy. However, such compounds are expensive and potentially harmful to human health and the environment. Hence, the development of nonfluorinated modifying agents or a decrease in their use is very important for the fabrication of environmentally friendly coatings. For this purpose, we [14, 16, 43] used stearic acid to modify TiO_2 particles or silica particles on roughened cotton textiles to make the textiles superhydrophobic.

4.3. Hydrophobization with nonfluorinated polymer

There are many polymers with low surface energy that can be used for hydrophobization. Ramaratnam *et al* [50] deposited a thin coating of a nonfluorinated hydrophobic polymer that contained 29 wt% styrene and 1.4 wt% reactive maleic anhydride groups on a poly(ethylene terephthalate) fabric covered with epoxidized silica nanoparticles. This resulted in an ultrahydrophobic textile surface. The coating was permanently anchored to the fiber boundary by the chemical attachment of the nanoparticles and polymers to the surface.

4.4. Hydrophobization with silicon/silane compounds

Alkyl silanes can react with moisture present on a substrate, allowing them to hydrolyze and condense to form a hydrophobic layer. A patent issued in 1945 detailed the use of an alkyl silane for the hydrophobization of paper or fabrics [51]. The silane reacted with moisture in the fibrous material, allowing it to hydrolyze and condense to form a hydrophobic layer. Gao and McCarthy have demonstrated that this method could be used for the production of an 'artificial lotus leaf' with polyester textiles as substrates [18]. Hoefnagels *et al* [41] rendered normally hydrophilic cotton superhydrophobic by introducing silica particles *in situ* to cotton fibers to generate a dual-size surface roughness, followed by hydrophobization with polydimethylsiloxane. This superhydrophobic textile exhibited a static water contact angle of 155° for a 10 μl droplet. The roll-off angle of water droplets depended on the droplet volume, ranging from 7° for a 50 μl droplet to 20° for a 7 μl droplet. Li *et al* [35] prepared superhydrophobic cellulose-based materials coupled with a transparent, stable and nanoscale polymethylsiloxane coating. They used a simple process involving chemical vapor

deposition followed by hydrolyzation and polymerization. In this method, polymethylsiloxane acted not only as a hydrophobization agent but also as a nanoscale silicone coating.

5. Applications

A number of products using the lotus effect are already commercially available or in the process of development. In addition, many patents have been granted for various possible applications of self-cleaning surfaces [52]. Most of these applications use the self-cleaning effect, especially of glasses (for architecture, automotive, optical sensor and other applications), roof tiles and other architectural materials. Additionally, sprays and paints that create clean surfaces (e.g. graffiti-resistant) have been proposed, as well as water-repellent textiles. Some agricultural applications were also discussed (e.g. pesticide additives with improved adherence to plant surfaces or increased penetration into the soil).

From a commercial point of view, the cleaning of windows is expensive and cumbersome, especially if the windows are on a skyscraper. Self-cleaning windows using the lotus effect have been introduced to the market by several companies. The commercial success of these windows remains to be seen [52, 53].

The research on superhydrophobic textile surfaces is driven by various functional applications. The following discussion will also cover how superhydrophobic coatings are used to improve the performance of conventional textile materials by surface modification, and how superhydrophobic modification brings about new functions to the textiles.

5.1. Water repellence

The problem of waterproofing surfaces, specifically fabrics, was first critically examined by Wenzel in 1936 [54].

In most studies, the waterproofing of textiles is considered a primary potential application of the superhydrophobic effect. Textiles with a superhydrophobic coating could be used as water-resistant apparel and would generally be useful for any kind of applications where textile surfaces are exposed to the environment. An advantage of superhydrophobic textiles is that the fibrous structure can be maintained while keeping the substrate breathable, which is preferable to traditional waterproof textiles treated with rubbers, plastics, sealing agents, or a conventional wet-chemical finish using fluorocarbons. Additional benefits of the superhydrophobic effect on textiles could include a plastron layer [34]. This thin layer of air forms on many natural superhydrophobic surfaces upon immersion in water. On the one hand, the ability to support a plastron layer would prevent wetting of the textile even upon full immersion in water; on the other hand, it would significantly reduce the frictional drag in water. Also, it is convenient for users to get their mobile marquees, awnings, umbrellas, etc with water shedding effect easily stored even after a shower.
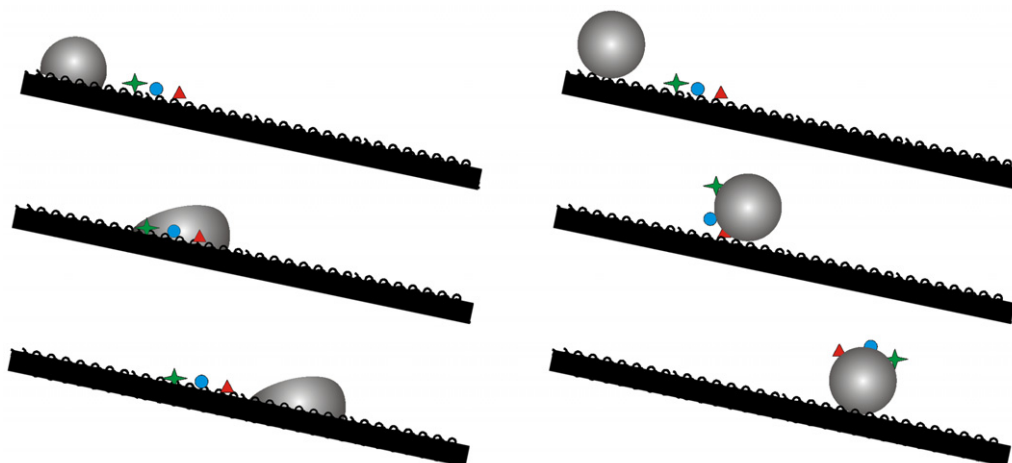
Figure 12. Water droplets rolling off substrates with a normal hydrophobic surface (left) and a self-cleaning superhydrophobic surface (right) through dust particles.

5.2. Self-cleaning

Superhydrophobic and self-cleaning surfaces with a high static contact angle above 150° and low contact angle hysteresis (the difference between the advancing and receding contact angles) play an important role in technical applications ranging from self-cleaning window glasses to paints and textiles, and including low-friction surfaces for fluid flow and energy conservation [6, 55–57].

Surfaces gradually become contaminated in a natural environment. Cleaning them requires much effort; additionally, surfactants are often applied with negative effects on the environment. The creation of substrates that can clean themselves or have anticontamination properties has long been a dream. 'Self-cleaning clothes' and the associated research have been a hot topic for several decades [58], and the technology for creating self-cleaning substrates has developed rapidly in recent years.

Superhydrophobic substrates with a self-cleaning property are prepared mostly on the basis of the lotus effect of plants. As illustrated in figure 12, when a droplet of water rolls off the surface of a superhydrophobic substrate, it removes the dust, whereas the dust remains on the normal surfaces.

Superhydrophobic surfaces with a self-cleaning effect have been fabricated by mimicking the behavior of the lotus leaf and other plants, which have rough surfaces combined with hydrophobic surface chemistry. Several approaches described in this review have been commercialized and transformed into proprietary technologies. For example, self-cleaning textile products, such as shirts, blouses, skirts and trousers, which shrug off ketchup, mustard, red wine and coffee [59], have already been produced.

STO Corp. (USA), a manufacturer of high-quality building materials, has been marketing an exterior paint since 1999 under the trade name Lotusan®. The product is a highly water-repellent surface similar to that of the lotus leaf. Its microstructure has been modeled on the lotus leaf to minimize the contact area for water and dirt. The surface additionally

offers high resistance to the growth of mold, mildew and algae [13].

With Mincor TX TT, BASF has made it possible to produce textiles with a genuine self-cleaning effect based on nanostructured surfaces [60]. This finishing material endows technical textiles with the same self-cleaning effect as the lotus leaf. Particles with a diameter below 100 nm embedded in a carrier matrix on the treated textile mimic the tiny papillae found on the surface of the plant leaves and repel water droplets. Dirt particles are carried along by the water droplets and are washed away without the need for detergents or scrubbing. In 2006, polyester awning fabrics finished with Mincor TX TT signaled the transition from the laboratory to practical applications, and fabrics for sunshades and sails treated with Mincor TX TT also show promise. The application of Mincor to washable fabrics such as cotton to produce dirt-repellent clothing is also expected.

Nano-Care [59] is a fabric finish developed by the inventor and entrepreneur David Soane and produced by his company Nano-Tex. Fabrics made from Nano-Care treated fibers or threads repel molecules of liquid, dirt, or perspiration. This idea was inspired by the fuzz on a peach and is called the Nano-Care effect. Nano-Care's 'fuzz' is made of minuscule whiskers and is attached to the cotton threads.

The Swiss firm Schoeller Textil AG developed a technology named NanoSphere [59]. In this technology, nanoscopic particles of silica or a polymer were attached on the clothing fibers, and these particles provide lotus like bumpy roughness, making textiles superhydrophobic and self-cleaning.

5.3. Anti-biofouling

Biofouling of underwater structures and ships' hulls, in particular, increases operational and maintenance costs [61, 62]. It can be reduced through underwater superhydrophobicity, i.e. forming a hydrophobic rough surface that supports an air film between itself and the water [63]. The reduction of the wetted area minimizes the probability that biological organisms encounter

a solid surface. The design of such surfaces should involve optimization between mechanical stability and minimal wetted area. The anti-biofouling properties of superhydrophobic coatings have been investigated [64]. Compared to normal substrates which fouled within a day, almost no micro-organisms attached to the superhydrophobic surfaces in the first weeks after immersion. However, after long exposure to a real marine environment, the antifouling property of the superhydrophobic coatings gradually deteriorated indicating that the long-term stability steel needs to be addressed [3].

5.4. Anticorrosion

The prospect of producing surfaces that repel water suggests huge opportunities in the areas of corrosion inhibition for metal components, chemical and biological agent protection for clothing, antifouling of marine vehicles and many other applications [65]. Given their strong water repulsion properties, superhydrophobic coatings are ideal for slowing the breakdown of the native metal oxide layer of metal substrates, and thus the corrosion of the aluminum layer underneath [65]. Zhang *et al* [66] utilized the intercalation of laurate anions by ion exchange with ZnAl-(layered double hydroxides)–NO_3^- film precursors on a porous anodic alumina/aluminum substrate to fabricate a hierarchical micro/nanostructured superhydrophobic film, which provided a very effective corrosion-resistant coating for the underlying aluminum. Liu *et al* [67] prepared stable superhydrophobic films with a contact angle of 151° on zinc substrates by a simple immersion technique into a methanol solution of hydrolyzed $1H,1H,2H,2H$-perfluorooctyltrichlorosilane for 5 days at room temperature followed by annealing at 130 °C in air for 1 h. The superhydrophobic film provided an effective corrosion-resistant coating for the zinc interface when immersed in an aqueous solution of NaCl (3%) for up to 29 days. By adding a zinc foil into the $1H,1H,2H,2H$-perfluorooctyltrichlorosilane/methanol solution which contained silicon or steel, superhydrophobic surfaces were formed on those silicon and steel surfaces [68].

5.5. Bifunction/multifunction

The next generation of superhydrophobic coatings must combine the already achieved self-cleaning properties with additional functionalities, such as optical transparency, in a coating that is made from inexpensive materials and is sufficiently durable for everyday use [69, 70]. Bifunctional or multifunctional superhydrophobic coatings might be preferable in terms of market potential.

Manca *et al* [22] fabricated durable superhydrophobic and antireflective surfaces by sol–gel processing using trimethylsilanized silica nanoparticles. The prepared surfaces showed excellent water repellency (contact angle = 168°) and a stable self-cleaning effect during 2000 h of outdoor exposure. Also, the nanotextured topology generated by the top layer of self-assembled nanoparticles produced a fair antireflection effect with more than a 3% increase in optical transmittance. Qu *et al* [71] fabricated a lotus-leaf-like

structured polyaniline film with stable superhydrophobic and conductive properties.

Textiles with more than one function have an increased value. Thus, we [43] produced superhydrophobic textiles with a UV-shielding property through incorporation of TiO_2 particles by titania sol coating. Tomšič *et al* [72] prepared water and oil repelling and antimicrobial finishes for cotton fibers from a commercially available fluoroalkylfunctional water-borne siloxane, nanosize silver particles and a reactive organic–inorganic binder. Vilčnik *et al* [73] fabricated hydrophobic and oleophobic sol–gel coatings with a long-lasting passive antibacterial effect for cotton fabrics without the addition of any antibacterial agent. The prepared fabrics have a long-lasting low surface energy, owing to the excellent adherence of the finishes to cotton fabrics and to the specific structure of the coatings, which included $1H,1H,2H,2H$-perfluorooctyltriethoxysilane.

The main cause of the passive antibacterial effect of the unwashed fabrics was the ability of the coatings to repel water. In fact, superhydrophobic surfaces have been used for anti-biofouling [3, 74] on submerged surfaces, such as ships' hulls, because of the lower ability of organisms to adhere to superhydrophobic surfaces. Superhydrophobic textiles might also find future application as antimicrobial coatings.

6. Outlook

There has been considerable research on superhydrophobic surfaces. However, there have been few reports on the robustness of superhydrophobic coatings and the durability of superhydrophobicity [3, 21]. There is still much work to be done for superhydrophobic surfaces to be incorporated into commercial products. Besides durability, issues such as large-area production and the availability and price of raw materials should also be taken into consideration. In the future, superhydrophobic surfaces based on novel materials, such as carbon nanotubes [75], fullerenes [76, 77], gold [78] and carbon fibers, might also be produced at a large scale once the price of these materials is reduced.

For self-cleaning surfaces, many publications focus only on removing dust by water, which is a complex problem. Firstly, the contamination could contain various components such as fly ash, water slurry, kitchen oil, etc. In this case, washable [40] or oil repellent surfaces [2, 79, 80] are preferable. Secondly, the surface might be contaminated with a smudge and might not function properly until it is removed. A lotus leaf repairs itself after it has been scratched because it has tiny wax crystals on the surface that regenerate. Self-healing materials have been prepared in other fields. In future, the practical applications of self-cleaning or contaminant-free surfaces [53] and the fabrication of self-cleaning surfaces with self-healing superhydrophobicity might be possible.

Finally, environmental issues should be taken into account when preparing superhydrophobic surfaces for everyday use. It has been recognized that some fluorochemicals and organic solvents have potential risks to human health and the environment and their use should be minimized.

Acknowledgments

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