

## FEATURE ARTICLE

## Long-lived superhydrophobic surfaces

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Prolonging the lifetime of superhydrophobic surfaces is required so that the materials can be used practically. Thus, great efforts have been made in designing surfaces that maintain micro- and nanoscaled hierarchical structures and low surface-energy property, which are necessary for superhydrophobicity, during use. It was demonstrated that improving surface mechanical strength to increase wear resistance helps maintain hierarchical roughness, retarding the loss of superhydrophobicity. Additionally, designing self-healing materials that can recover their structure and/or properties when damaged has been suggested and demonstrated to sustain the superhydrophobicity of surfaces. This review focuses on recent advances in developing mechanically durable, corrosion-resistant, self-healing, and easily repairable superhydrophobic surfaces, which will enable prolonged lifetime of superhydrophobicity for practical applications in the future.

## 1 Introduction

Superhydrophobic surfaces have attracted significant attention within the scientific community as well as the industrial world over the last two decades. These surfaces, which have contact angles greater than 150°, promise a wide range of uses in non-wetting,<sup>1–5</sup> self-cleaning,<sup>6–12</sup> anti-fogging,<sup>13</sup> anti-icing,<sup>14–20</sup> buoyancy,<sup>21–23</sup> corrosion-resistant,<sup>24–28</sup> anti-biofouling,<sup>29</sup> oil–water separation,<sup>30–35</sup> low adhesion,<sup>11,36,37</sup> and drag-reducing<sup>38–40</sup> applications. A considerable amount of work has been carried out to

study the mechanisms and principles of superhydrophobicity. Several reviews on fundamental theories about wetting phenomena and experimental studies for applications of superhydrophobic surfaces have appeared in the literature.<sup>9,41–62</sup> Most importantly, much attention has been paid to the durability of superhydrophobic materials, especially after the work by Genzer and Efimenko<sup>63</sup> which focused on creating long-lived superhydrophobic surfaces. The combination of the surface chemical composition and the topographic structure has been shown to be responsible for the superhydrophobicity of the surfaces. Consequently, several ways have been put forward to improve the durability of superhydrophobic surfaces, including enhancement of mechanical stability, improvement of corrosion-resistance, self-healing of topographic structures and self-repairing of surface chemical properties.

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are focused on the design and fabrication of superhydrophobic materials with various surface functionalities, and organic–inorganic nanocomposite functional coatings.



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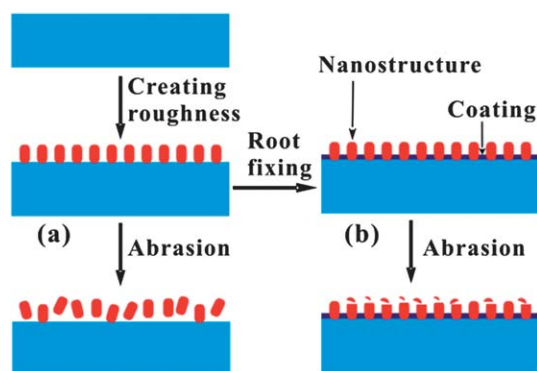
include synthesis, characterization and properties of organic–inorganic nanocomposite materials, and development of functional coatings and films.

This review mainly focuses on the main approaches to mechanically durable, corrosion-resistant, self-healing, and easily repairable superhydrophobic surfaces as well as investigations on durability test on superhydrophobicity. Other review articles can be referred to for theoretical studies, modeling, and other investigations on superhydrophobic surfaces. Considering the rapidly expanding body of literature in the field, the list of examples provided in this review is by no means exhaustive. Representative works were selected from the most recent literature available with the intent to give readers a critical discussion of the fabrication and properties of long-lived superhydrophobic surfaces. Also personal perspectives on future research concerning the construction of surfaces with long-lived superhydrophobicity are briefly addressed.

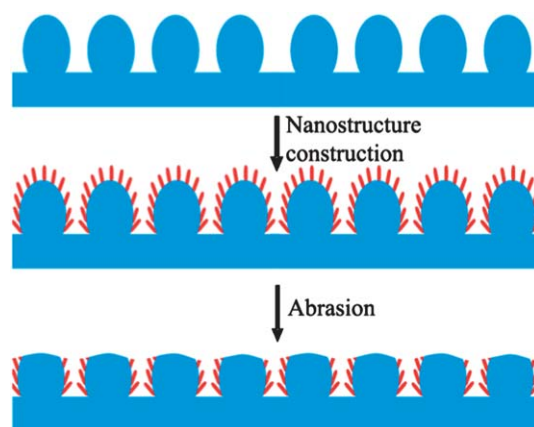
## 2 Mechanically durable superhydrophobic surfaces

Construction of rough structure is one key to superhydrophobic surfaces. Thus the mechanical stability of the topographic structure significantly affects the durability of superhydrophobicity. Most studies constructed roughening structures by decorating substrates with nanostructured layers. We refer to this approach as creating roughness from extra-substrate nanostructures. In this approach, the interaction between the substrate and the nanostructure layers crucially affects the stability of the surface structure. If the interaction is weak, the nanostructures may be removed under abrasion, as shown in Fig. 1(a), making the surface lose superhydrophobicity. However, if the interfacial interaction between the substrates and the structural layers is strengthened, such as by coating to keep nanostructures fixed, durable surfaces can be obtained. In this case, the surface roughness of the nanostructures can only be broken completely by shearing wear over long times, as shown in Fig. 1(b).

When the nanostructures are fixed stably on the substrate, the durability of superhydrophobicity depends mainly on the mechanical property of the nanomaterials. However, most of the nanoscale materials are more fragile than the microscale ones on surfaces containing both micro- and nanostructured structures. Therefore, when fragile nanostructures are used to



**Fig. 1** The effect of wear on surfaces with (a) weakly attached nanostructures and (b) strengthened nanostructures with root fixed by coating.

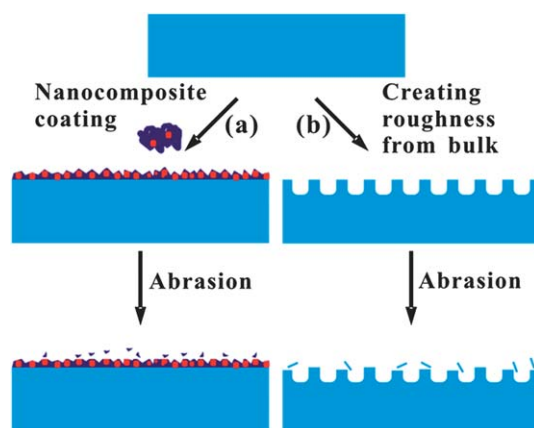


**Fig. 2** The effect of wear on a surface with mechanically stable microscales decorated by nanostructures, most of which are unaffected by wear.

enhance the roughness and/or to lower the surface-energy of microscale structures, the microroughness should be optimized to improve its mechanical stability and keep the nanoroughness protected. This concept was proposed by Verho *et al.*<sup>57</sup> and is illustrated in Fig. 2.

In addition to incorporating nanostructures onto substrates, nanocomposite coating with low surface-energy polymers as film forming agents and nanoparticles as surface roughening materials was also used to construct superhydrophobic surfaces. In this way, the durability of the roughening coating depends on the wear resistant ability of the polymer, the compatibility between nanoparticles and the polymer, and the adhesion ability of the polymer to the substrate. Consequently, improving the wear resistance of the polymers, as shown in Fig. 3(a), is crucial to prolonging the lifetime of superhydrophobicity.

Additionally, microscopic roughness could be created from the bulk matrix of materials at the surface. The roughening structure is part of the substrate matrix as a whole, which avoids the interfacial problems in other methods that introduce extra materials onto substrates. In this case, the surface becomes smooth and the surface roughness gets lost only if the



**Fig. 3** The effect of wear on surfaces with nanostructures by (a) nanocomposite coating on the substrate and (b) etching on the surface of bulk matrix of the substrate.

nanostructures are worn away, as shown in Fig. 3(b). Therefore, structures created directly from substrates generally have strong adherence and mechanical stability.<sup>64</sup>

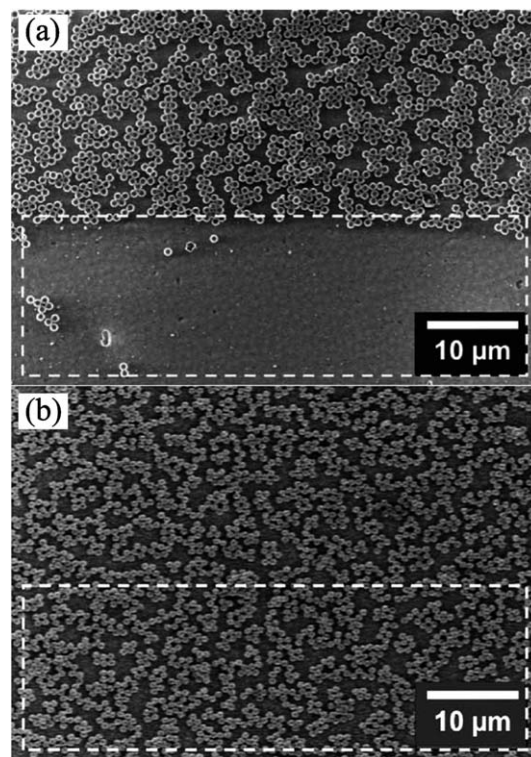
### 2.1 Creating roughness from extra-substrate nanostructures for superhydrophobic surfaces

Many studies have reported on roughening substrates with extra-substrate nanostructures, such as nanoparticles,<sup>65–72</sup> nanorods,<sup>20,72–74</sup> and nanowires.<sup>1,75,76</sup> However, only a few studies have focused on the stability of the nanostructural layer which affects the durability of superhydrophobic surfaces.

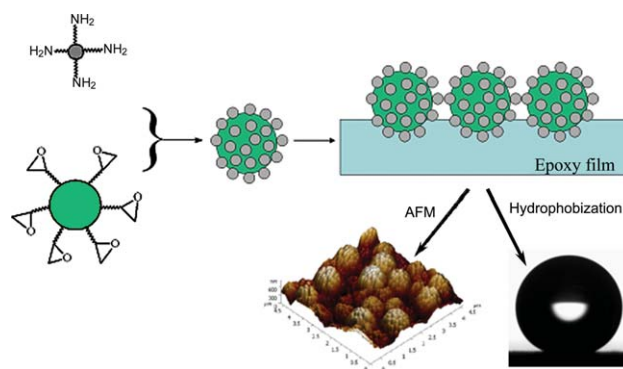
Ling *et al.*<sup>67</sup> created a superhydrophobic surface by dip-coating 60 nm SiO<sub>2</sub> nanoparticles onto an amine-terminated self-assembled monolayer glass/silicon oxide substrate. This was followed by sintering of the nanoparticle coated substrate under O<sub>2</sub> at 1100 °C and chemical vapor deposition of a fluorinated adsorbate. A peel test using a pressure-sensitive adhesive tape showed that the coverage of nanoparticles on the substrate was totally removed before sintering, but remained on the substrate after sintering. This was attributed to the chemical and thermal bonding of nanoparticles onto the SiO<sub>2</sub> substrate,<sup>41</sup> improving the stability of the nanoparticle layer on the substrate.

Deng *et al.*<sup>68</sup> fabricated superhydrophobic surfaces based on porous silica capsules from polystyrene-microparticle–silica-nanoparticle core–shell raspberry-like particles. The neighboring particles were chemically bound to each other and to the surface *via* silica bridges by hydrolysis and condensation of TEOS, which were catalyzed by ammonia in a CVD process of TEOS at 350 °C, thus making the nanostructures fixed on the surface. Therefore, the robust surface can withstand the peeling of tape pressed with approximately 10 kPa to the substrate. In contrast, almost all particles were removed by peeling the tape off the surface when particles were attached only by van der Waals interactions. SEM images of the two different surfaces are shown in Fig. 4. This further shows that fixing nanostructures on substrates plays an important role in the durability of superhydrophobic surfaces.

However, high temperature sintering or treatment of substrate is not suitable for organic substrates, such as plastics, polymer films, and textiles. Recently, chemical reactions between substrate and nanoparticles were used to enhance the interaction between substrate and roughening layers. As shown in Fig. 5, Ming *et al.*<sup>66</sup> 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. In this way, the obtained superhydrophobic surface should be stable, although its stability was not reported.

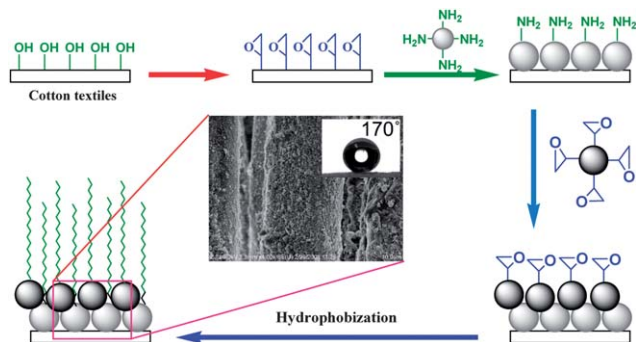


**Fig. 4** SEM images of superhydrophobic surfaces that were partially exposed to double sided tape (white boxes indicate the exposed areas). (a) Particles were attached to the surface by van der Waals interaction only. (b) Particles were chemically bound to the surface by silica bridges. Reproduced with permission.<sup>68</sup> Copyright 2011 Wiley-VCH.



**Fig. 5** Preparation of superhydrophobic films based on covalent assembly yielding raspberry-like particles. Adapted with permission.<sup>66</sup> Copyright 2005 American Chemical Society.

Similarly, Amigoni *et al.*<sup>69</sup> 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 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. To maintain nanoparticle durability on fibers, Xue *et al.*<sup>70</sup> utilized covalent bonding between substrate

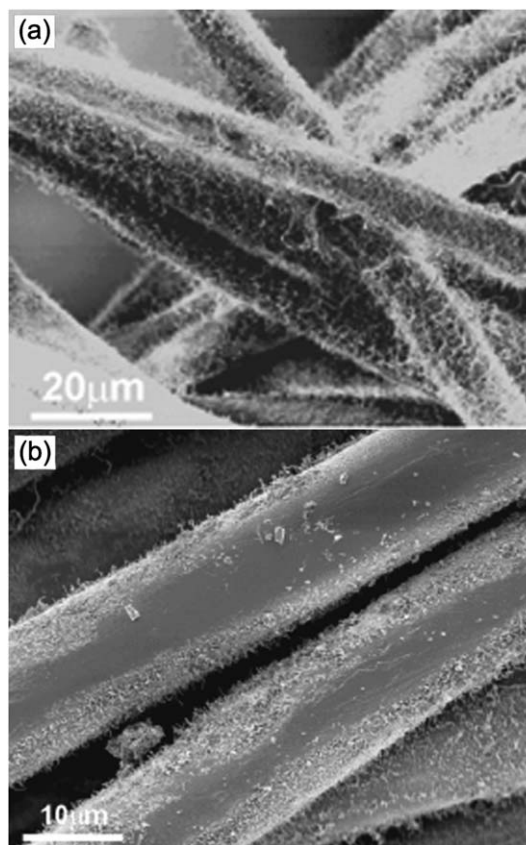


**Fig. 6** Superhydrophobic surfaces on cotton textiles by complex coating of silica nanoparticles and hydrophobization. Adapted with permission.<sup>70</sup> Copyright 2009 Elsevier B.V.

and nanoparticles in a complex coating process to construct robust roughness on textiles, shown in Fig. 6. The contact angle (CA) of the obtained surface reached 170°. In the process, the bonds were created by chemical reactions between epoxy groups and amino groups, which were pre-induced on cotton fibers and SiO<sub>2</sub> nanoparticles, respectively. The first layer of nanoparticles was covalently bonded to the cotton fibers, and the other layers of SiO<sub>2</sub> assembly were deposited by the same mechanism. SEM images showed that the nanoparticles remained stable on the fibers after 1 hour sonication in ethanol, with a CA of 165°.

These works demonstrated that it is possible to obtain durable superhydrophobic surfaces by solving the interfacial problems between the substrates and the nanostructural layers, as mentioned in Fig. 1(b). However, protecting the nanostructures from wear, as shown in Fig. 2, is also a good way to fabricate superhydrophobic surfaces. Zimmermann *et al.*<sup>1</sup> grew a layer of superhydrophobic silicone nanofilaments on textile fibers to obtain a hierarchically rough superhydrophobic fabric, shown in Fig. 7(a). Although the nanofilaments are very fragile and can easily be wiped away, the coated textile kept its superhydrophobic character even after continuous rubbing with a skin simulating friction partner under a force of 5 N. The effect of wear was quantified with the water shedding angle, which is the tilt angle above which a water drop is shed by the surface after falling from a predefined height. Results showed that 1450 cycles of wear led to an increase of the shedding angle from 2° to 25°, illustrating that the abrasion makes the surface more sticky towards water. The SEM image in Fig. 7(b) shows that nanofilaments were worn off from the contact surfaces but remained intact elsewhere. It should be noted that large-scale production of superhydrophobic surfaces by this strategy had been realized.<sup>77</sup>

Another demonstration of this concept was presented by Xiu *et al.*,<sup>78</sup> who prepared two-tier roughness on silicon by first etching with KOH to create microscale pyramids and then using Au nanoparticle catalyzed HF/H<sub>2</sub>O<sub>2</sub> etching to fabricate nanostructures on the pyramids. This was followed by a fluorination treatment to render the hydrophilic silicon surface hydrophobic. The durability of the surface features was tested by drawing the sample on a TechniCloth wipe under a load of 3.5 kPa. Despite an increase in contact angle hysteresis the



**Fig. 7** PET fabric coated with nanofilaments (a) before and (b) after a wear test. Reproduced with permission.<sup>1</sup> Copyright 2008 Wiley-VCH.

surface remained non-wettable, showing that the microscale pyramids protected the nanoscale features on the walls of the pyramids.

## 2.2 Nanocomposite coating for superhydrophobic surfaces

Nanocomposite coating is an important method to produce rough polymer films. This is done by incorporating inorganic nanoparticles for surface roughening and polymers for film forming or nanoparticle binding,<sup>53,65,79</sup> as shown in Fig. 3(a). SiO<sub>2</sub> nanoparticles have been most frequently used to provide the nanostructure,<sup>65,80–83</sup> although other nanomaterials such as ZnO,<sup>65,79,84,85</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>86</sup> silver,<sup>87,88</sup> carbon nanotubes<sup>89–91,92</sup> and boehmite<sup>93</sup> have also been used. Also, in addition to polydimethylsiloxane (PDMS) or modified PDMS,<sup>5,94</sup> other hydrophobic polymers<sup>14,82–84,89,90,95</sup> were used in the preparation. The manufacture of such coatings presumes the combination of chemical hydrophobization with the creation of a surface texture.<sup>96</sup> Therefore, when low surface-energy polymers are used, durable superhydrophobic surfaces can be obtained without post-hydrophobization.

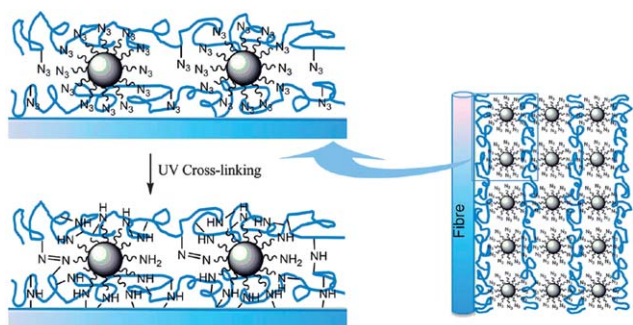
Cui *et al.*<sup>94</sup> prepared superhydrophobic surfaces with multi-scale nano/microstructures on epoxy paints by a three-step procedure. This includes sandblasting to construct microstructures, anchoring nano-SiO<sub>2</sub> to construct nanostructures, and dip-coating with epoxy adhesive modified by aminopropyl terminated PDMS to reduce the surface-energy. The

superhydrophobic surface also showed excellent stability against high speed scouring tests, soaking in neutral and basic aqueous solutions, and common organic solvents such as toluene and ethanol.

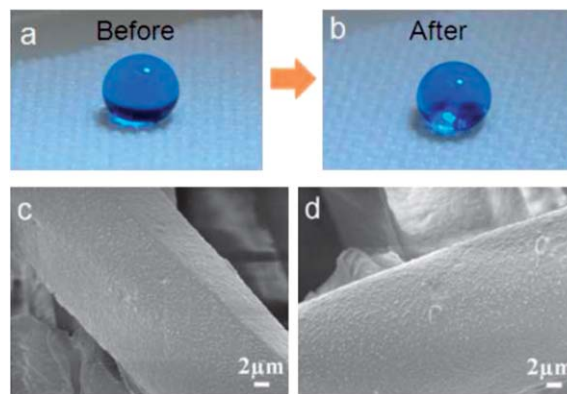
In nanocomposite coating, the interactions between substrate, nanomaterials, and polymer are significant in affecting the superhydrophobicity of surfaces. Zhao *et al.*<sup>97</sup> functionalized silica nanoparticles and poly(allylamine hydrochloride) (PAH) with highly photoreactive phenyl azido groups. They then utilized the azido-terminated silica nanoparticles as negatively charged building blocks and azido-grafted PAH as polycations for layer-by-layer electrostatic assembly to produce photoreactive silica nanoparticle/polycation multilayers on cotton fabrics. After coating, UV irradiation was used to induce covalent cross-linking within the multilayers as well as to anchor the multilayer film onto the organic substrate. This occurred through azido photochemical reactions including C–H insertion/abstraction reactions with surrounding molecules and dimerization of azido groups, as shown in Fig. 8. In the case of 5.5 layers of PAH-N3/silica-N3, a uniform layer of silica nanoparticles was observed on the cotton fibers. The superhydrophobicity of cotton fabrics was durable against acids, bases, and organic solvents, as well as repeated machine wash.

Inspired by tyre, a classic nanocomposite, Zhou *et al.*<sup>5</sup> used PDMS filled with fluorinated alkyl silane (FAS) functionalised silica nanoparticles and FAS to coat fabrics and investigated the durability of the superhydrophobic fabrics. They found that a crosslinked elastomeric thin coating was formed on fibers, which possessed a nanocomposite structure with a rough and low free-energy surface endowing fabrics with highly durable superhydrophobicity. The washing durability was evaluated by a standard procedure (AATCC Test Method 61-2006 test no. 2A). Increasing laundry cycles slightly decreased the CA and increased the sliding angle (SA). Both changes in CA and SA were less than 5° after 500 washing cycles, indicating the excellent durability to washing. SEM images revealed that the coating surface still retained its particulate morphology, even after 500 cycles of repeated washing (Fig. 9).

In addition, the abrasion resistance of the superhydrophobic surfaces was evaluated by the Martindale method using untreated fabric to simulate actual damage. The test was performed with separate loaded pressures of 9 kPa and 12 kPa,

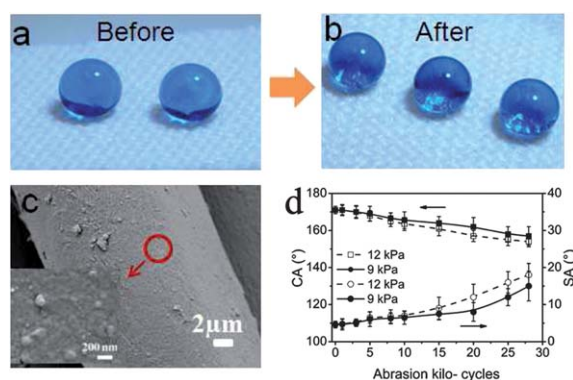


**Fig. 8** Schematics for the UV cross-linking of the PAH-N3/silica-N3 multilayers. Reproduced with permission.<sup>97</sup> Copyright 2012 American Chemical Society.



**Fig. 9** Photos of water droplet (10  $\mu$ L) on (a) the pristine coated polyester and (b) after 500 laundry cycles; SEM images of the coated fabric (c) before and (d) after 500 laundry cycles. Reproduced with permission.<sup>5</sup> Copyright 2012 Wiley-VCH.

which are the pressures used to evaluate coated fabrics for apparel and heavy duty upholstery usages, respectively. The changes in CA and SA with abrasion cycles are shown in Fig. 10(d). The CA remained at 170° after the first 2000 cycles under both pressure conditions. Although the CA became smaller with a further increase in abrasion cycles, the coated polyester fabrics can withstand at least 28 000 cycles of abrasion damages without losing their superhydrophobicity. After 28 000 cycles of abrasion under 12 kPa, water droplets on the fabric surface still show a CA above 150° and the nanoscale roughness can still be observed (Fig. 10). In comparison, the SA was more sensitive to the abrasion cycles. After 20 000 cycles of abrasion, the rate of SA change increased slightly. Besides the excellent washing and abrasion durability, the coated fabric can also withstand boiling water without changing its superhydrophobicity. These tests and further investigation demonstrated that the fluoroalkyl silane modified silicone rubber-nanoparticle composite coating showed remarkable durability against strong acid, strong alkali, repeated machine washes, boiling water, and severe abrasion damages, whilst retaining its superhydrophobicity. According to the report, this durable superhydrophobic coating was not limited to polyester fabric,



**Fig. 10** Water droplets (10  $\mu$ L each) on (a) the coated fabric and (b) after 28 000 abrasion cycles; (c) SEM image of the coated fabric after 28 000 abrasion cycles (loading pressure: 12 kPa); (d) CA and SA as functions of abrasion cycles under different loading pressures. Reproduced with permission.<sup>5</sup> Copyright 2012 Wiley-VCH.

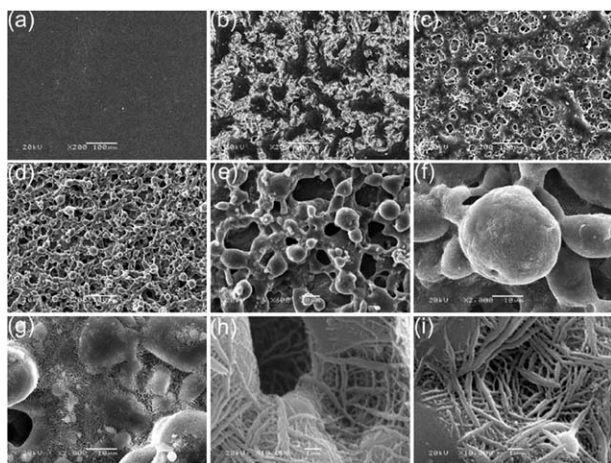
but could also be formed on other fibrous materials such as cotton and wool.

Alternatively, rough structures could also be obtained by phase change of polymers in the coating process to achieve stable superhydrophobic surfaces on substrates. Luo *et al.*<sup>95</sup> fabricated poly(tetrafluoroethylene)/poly(phenylene sulfide) (PTFE/PPS) superhydrophobic coating surfaces on engineering materials such as stainless steel and other metals by using PTFE and PPS in mixed solvent. The resulting surface possessed both micrometer- and nanometer-scale binary structure roughness (Fig. 11) as well as the lowest surface-energy hydrophobic groups ( $-\text{CF}_3$ ). It showed long-term stability over a wide pH range, not only for pure water, but also for corrosive liquids, such as base, and salt solutions. Moreover, the obtained surfaces possess very good cohesive strength, and high- and low-temperature resistance.

Nanocomposite rough structures made with durable polymers and improved interactions between nanoparticles, polymers, and substrates can achieve stable and robust coatings, which will facilitate the development of long-lived superhydrophobicity of surfaces.

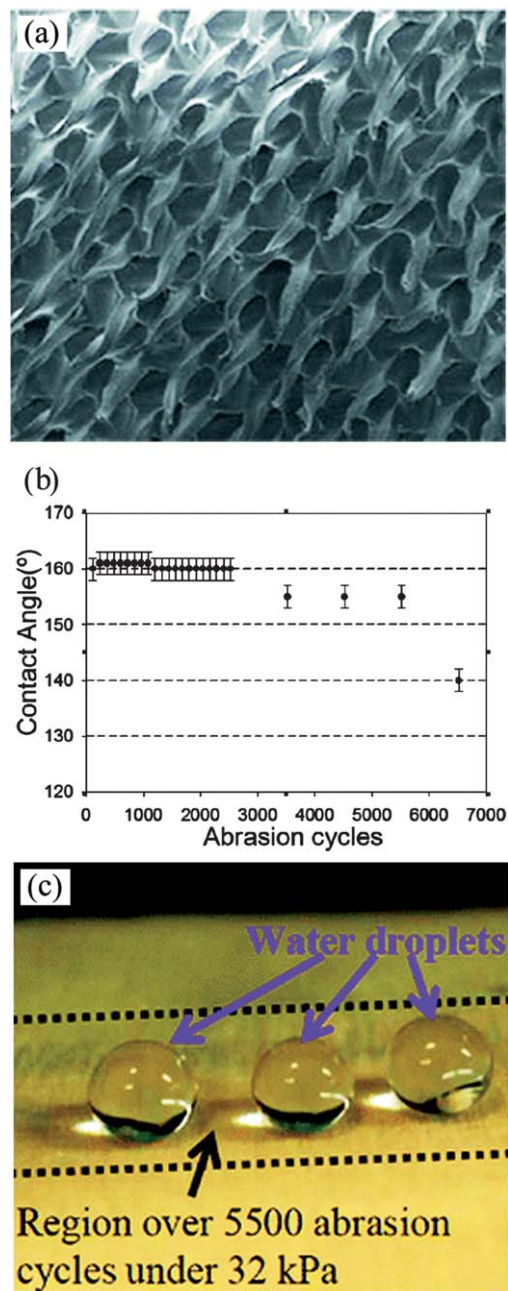
### 2.3 Roughening bulk materials at the surface for superhydrophobicity

Surface roughness could also be created directly from the bulk materials at the surface, resulting in hierarchical structures monolithic with the bulk substrate. These roughening structures possess strong adherence and mechanical stability, resulting in superior durability of superhydrophobicity compared to coatings which produce phase interface between the rough layer and the substrate. This strategy includes chemical etching,<sup>25,28,99–104</sup> electrochemical machining,<sup>105,106</sup> plasma texturing<sup>107–111</sup> and laser ablating<sup>112–114</sup> on metal, alloy, or polymer substrates. Templating polymers with artificial<sup>115–117</sup> or natural templates<sup>37,118,119</sup> was also conducted to construct predefined micro/nanostructures with the same phase as that of the substrate.



**Fig. 11** SEM images at different magnifications of surface microstructures. Pure PPS coating (a), PTFE/PPS coating (b), PTFE/PPS coating (c) with addition of  $(\text{NH}_4)_2\text{CO}_3$  solution. (d–i) PTFE/PPS superhydrophobic coating with addition of nonionic surfactant and  $(\text{NH}_4)_2\text{CO}_3$  solution. Reproduced with permission.<sup>95</sup> Copyright 2008 Wiley-VCH.

Xu *et al.*<sup>115</sup> reported a simple and inexpensive lamination templating method to create superhydrophobic surfaces of low density polyethylene (LDPE) with excellent abrasion resistance and water pressure stability. To fabricate the surfaces, polyethylene films were laminated against woven wire mesh templates. After cooling, the mesh was peeled from the polymer creating a 3D array of ordered polymer microposts on the polymer surface, as shown in Fig. 12(a). The resulting texture is monolithic with the polymer film and requires no chemical



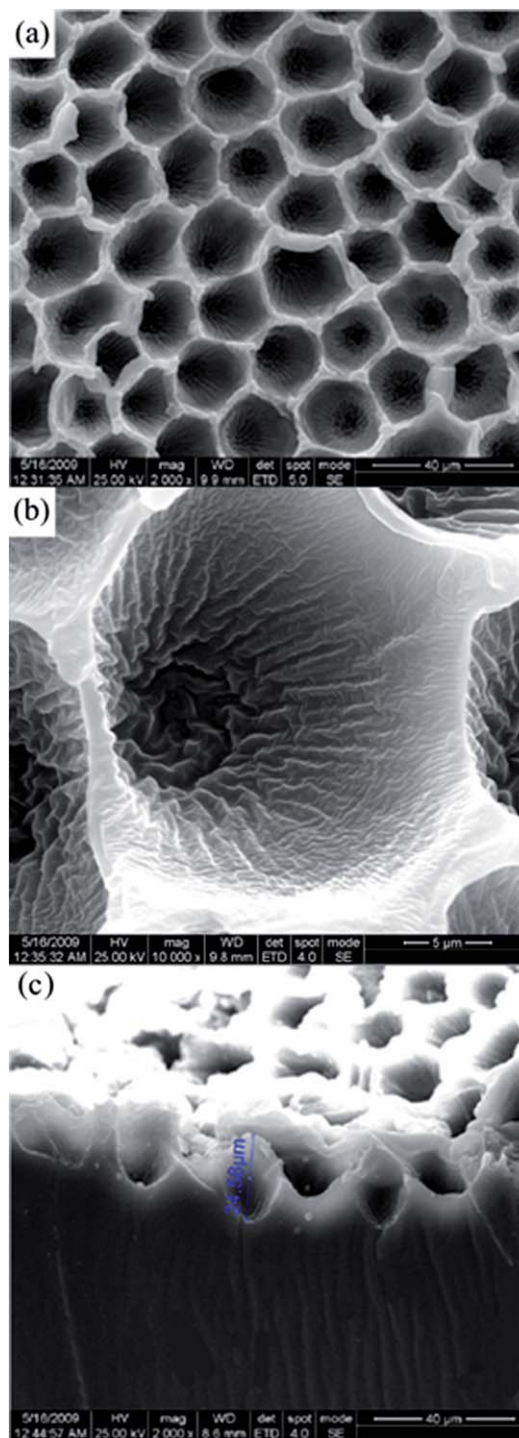
**Fig. 12** (a) SEM image of the lamination-templated surface structure; (b) water contact angle of superhydrophobic surface as a function of abrasion cycles using the Taber reciprocating abramer with a pressure of 32.0 kPa; (c) water droplets on the lamination-templated superhydrophobic LDPE surface after 5500 abrasion cycles under 32 kPa. Reproduced with permission.<sup>115</sup> Copyright 2011 American Chemical Society.

modification to exhibit superhydrophobicity. By controlling lamination parameters and mesh dimensions, polyethylene surfaces were fabricated that exhibited static contact angles of  $160^\circ$  and slip angles of  $5^\circ$ . Chemical and mechanical stability was evaluated using an array of manual tests as well as a standard reciprocating abraser test. Testing was performed with a loaded pressure of 32.0 kPa and a linear abrasion speed of  $8 \text{ cm s}^{-1}$ . The change in static CA of the superhydrophobic surface with increasing abrasion cycles is shown in Fig. 12(b). As seen in this figure, the static CA remained essentially unchanged at  $160^\circ$  over the first 2520 abrasion cycles and then decreased slowly to  $155^\circ$  with increasing cycles. The surfaces remained superhydrophobic after more than 5500 abrasion cycles at a pressure of 32.0 kPa, as shown in Fig. 12(c). In addition, the surface remained dry after immersion into water for 5 h at 55 kPa.

Su *et al.*<sup>116</sup> reported the creation of a superhydrophobic surface comprised of a polyurethane elastomer through casting a polyurethane precursor with hydroxyl-terminated PDMS as the low surface-energy material on a porous Al template. Friction testing demonstrated that the surface showed superhydrophobic and abrasion resistance properties with a contact angle as high as  $165.1^\circ$ . The CA still remained greater than  $150^\circ$  even after being loaded with 2945.7 Pa and rubbed for 10 000 times at  $18 \text{ cm s}^{-1}$ . Micro-protuberances on surfaces are easily deformed or broken during a friction cycle because protuberances are loaded with pressure and shear force. Elastic micro-protuberances will deform and fill in micro-concaves and the deformation can rebound when the load is withdrawn. However, for other materials, the micro-protuberances were either deformed into micro-concaves without rebounding or broken and formed rigid particles. Therefore, the permanent deformation and grinding defects on the polyurethane film were mainly caused by adhesive abrasion and fatigue abrasion resulting from an alternating force during the friction cycle.

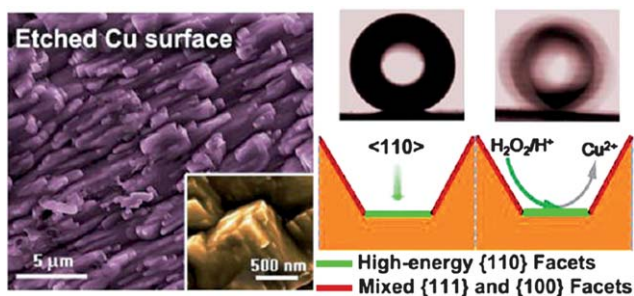
Yuan *et al.*<sup>118</sup> prepared a honeycomb-like superhydrophobic PDMS surface using a template method. Numerous nanostructures can be observed in each honeycomb-like hole, as shown in Fig. 13(a), with a complementary topographic surface structure of the natural rose petal. The walls are monolithic with the bulk PDMS substrate with a height of about  $24 \mu\text{m}$ , as shown in Fig. 13(b). Durability and wear resistance tests demonstrated that the superhydrophobic polydimethylsiloxane surface showed high stability in the pH range from 1 to 14. The superhydrophobic PDMS surface also maintained high superhydrophobicity and the surface microstructures remained unchanged even after 30 times sliding friction tests without a lubricant at a speed of  $0.5 \text{ m s}^{-1}$  under the loads of 5–20 N in air. Also, no decrease in water contact angle was observed after storage in an ambient environment for 6 months.

Liu *et al.*<sup>98</sup> fabricated a superhydrophobic Cu surface by selective etching of high-energy facets at an ultra low etching rate in  $\text{H}_2\text{O}_2/\text{HCl}$  solution, resulting in the formation of dual-scale convex polyhedral protrusions with regular shapes, as shown in Fig. 14. The mechanical strength of the superhydrophobic Cu surface was evaluated by ultrasonic treatment in water. After ultrasonication for 1 h, the resultant surface exhibited a mean CA of  $165^\circ$ . After the superhydrophobic

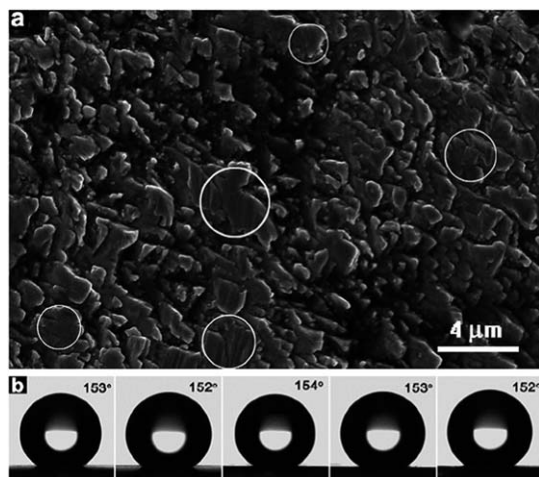


**Fig. 13** SEM images of (a) the as-prepared honeycomb-like superhydrophobic PDMS surface, (b) is a single magnified honeycomb-like hole on the as-prepared superhydrophobic PDMS surface, (c) is the cross-sectional view of the as-prepared honeycomb-like superhydrophobic PDMS surface. Reproduced with permission.<sup>118</sup> Copyright 2010 Elsevier B.V.

surface was subjected to a normal pressure ( $\sim 5 \text{ kPa}$ ) and slid on a common cotton fabric ( $40 \text{ s} \times 40 \text{ s}$ ) by 25 cm in one direction for the abrasion test, some tips of the convex polyhedral protrusions were worn off, resulting in mean water CA of  $153^\circ$ , as shown in Fig. 15. The decrease of the CA can be



**Fig. 14** Etched Cu surface and the schematic illustration for the formation of polyhedral microprotrusions via the selective etching of high-energy {110} facets. Reproduced with permission.<sup>98</sup> Copyright 2012 American Chemical Society.



**Fig. 15** (a) SEM image of the superhydrophobic Cu surface after the abrasion test. The white circles represent the typical areas which are worn away. (b) The photographs of a 5  $\mu\text{L}$  water droplet on the superhydrophobic Cu surface after the abrasion test. The mean value of the five CAs is about  $153^\circ$ . Reproduced with permission.<sup>98</sup> Copyright 2012 American Chemical Society.

ascribed to the partial loss of the surface roughness and the adsorbed stearic acid molecules. The chemical stability of the superhydrophobic surface was also characterized by immersing the sample in aqueous solutions with various pH values. After immersion for 72 h, the resultant superhydrophobic surface showed a CA of more than  $158^\circ$  for all pH solutions.

Lee *et al.*<sup>103</sup> reported that morphological change induced by an oxidation–reduction reaction can be effectively employed for producing superhydrophobic copper without use of any hydrophobic agents. By thermal oxidation of copper, needle-shaped CuO nanowires were grown on the copper substrate. Subsequent reduction led to wavy Cu nanowire structures, which exhibited superhydrophobic properties with a contact angle of over  $160^\circ$  and a sliding angle of less than  $2^\circ$ . Mechanical stability was evaluated by pressed contact, adhesion by using Scotch tape, and hardness by using a pencil. It was found that the needle-shaped CuO nanowires were rather mechanically weak and brittle and easily broken or removed. In contrast, the wavy Cu nanowires were mechanically stable and flexible, thus retaining superhydrophobicity after tests. This might be because exfoliation occurred at the interface between

the copper substrate and the CuO surface layer due to their chemical structure differences. However, reduction led to the inside of the structural surface having the same chemical composition or the same phase as the copper substrate, eliminating the exfoliation problem.

These reports demonstrated that changing the surface morphology by creating roughness directly from the bulk substrate can be utilized to produce superhydrophobic surfaces with good mechanical stability.

### 3 Corrosion-resistant superhydrophobic surfaces

In addition to physical processes, such as pressure, abrasion, or peeling, corrosive or chemical processes, such as weathering, chemical etching, or irradiation, can also cause loss of superhydrophobicity due to the decomposition of low surface-energy materials. This must be taken into consideration when materials are designed for specific practical application. For example, electrolyte corrosion might occur when the materials are to be used on hulls of ships that contact sea water. Photodegradation of low surface-energy substances under strong sunlight can occur in an outdoor environment, especially with photocatalytic materials. Once the hydrophobic components are damaged, loss of superhydrophobicity ensues.

Recently, researchers have begun to examine corrosion resistance of the superhydrophobic materials and have prepared anti-corrosive superhydrophobic surfaces for specific applications. There are currently no standard methods to evaluate the corrosion resistance of superhydrophobic surfaces. However, superhydrophobic coatings showing remarkable durability against longtime storage or outdoor exposure,<sup>10,95,120,121</sup> strong acids,<sup>92,94,95,100,120,122–126</sup> strong alkalis,<sup>95,97,98,103,120,122,123,125,126</sup> boiling water,<sup>97</sup> sea water or NaCl solution,<sup>24,27,28,95,127,128</sup> common solvents,<sup>129</sup> and UV-light<sup>31,130–134</sup> have been fabricated.

A superhydrophobic treatment could be a promising technology to improve anticorrosion performance of materials because it inhibits the contact of the surface with water and environmental humidity.<sup>27</sup> Therefore, extending the lifetime of superhydrophobicity might help prolonging the lifespan of superhydrophobic surfaces. Liu *et al.*<sup>128</sup> fabricated a superhydrophobic surface on copper substrate with *n*-tetradecanoic acid and examined the corrosion-resistant performance in seawater by electrochemical measurements. Zhang *et al.*<sup>24</sup> prepared superhydrophobic layered double hydroxide coatings on aluminum and investigated the corrosion resistance of the coating by dc polarization. The superhydrophobicity of the coatings provided long-term corrosion protection of the coated aluminum substrate and provided an effective barrier to aggressive species. Similarly, a superhydrophobic surface was fabricated<sup>127</sup> on anodized aluminum by modifying myristic acid to improve the corrosion resistance of aluminum.

In addition to engineering materials such as steel, copper, zinc, aluminum, and some alloys,<sup>24,27,95,99,103,120,124,127–129,135</sup> the corrosion-resistance of superhydrophobicity in organic materials, such as textiles,<sup>5,97,131,132,134,136</sup> has also been investigated.



## 4 Self-healing superhydrophobic surfaces

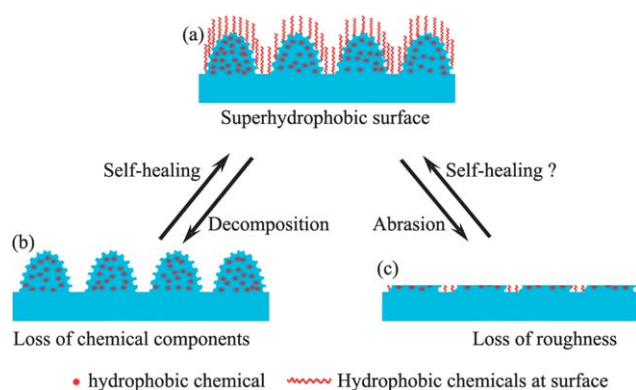
Natural superhydrophobic plant leaves and insect wings can remain effective over their lifetime through continuous biological renewal and self-healing of the surface.<sup>57,58,137–139</sup> Mimicking this self-healing functionality in man-made superhydrophobic surfaces<sup>58,140</sup> might prolong the lifetime of superhydrophobicity.

The key to superhydrophobic surfaces lies in the combination of the surface chemical compositions and the topographic structures. Endowing these surfaces with the ability to regenerate the surface roughness or/and restore the hydrophobic components can provide an efficient way to obtain long-lived superhydrophobicity. To produce self-healing in superhydrophobic materials, low surface-energy chemicals are usually stored inside reservoirs in the roughening structures, as shown in Fig. 16. When the hydrophobic chemicals decompose (Fig. 16(b)), the ones inside the reservoirs would be released and migrate toward the outermost surfaces, repairing the surface chemical components.

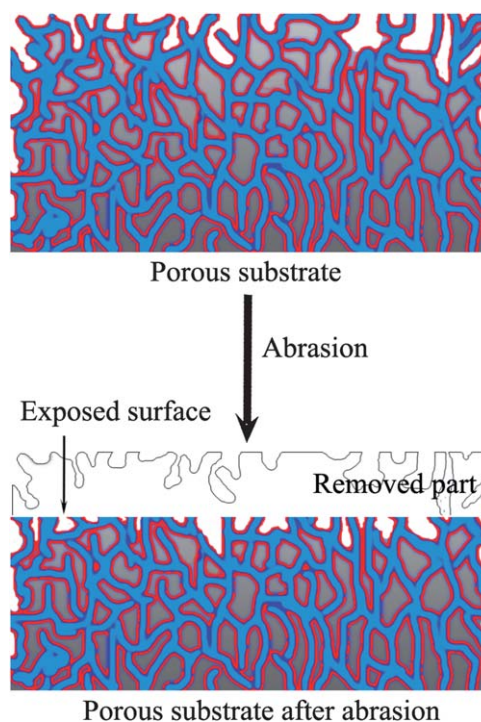
However, when the roughening structures become smooth due to abrasion, as shown in Fig. 16(c), it is impossible for the man-made substrate to restore the original roughening structures due to the conservation of mass. Wearing occurs very often for materials used in everyday life. Therefore, exposing new roughening structures during the rubbing process provides a good way to maintain roughness if the original structures of the surface are destroyed. It has been demonstrated that porous substrates could be designed to form fractal-like networks, with rough structures in the cross-section.<sup>141</sup> Superhydrophobic porous surfaces containing hydrophobic chemicals in all the pores throughout the substrate might maintain superhydrophobicity after strong abrasion. Removing a layer of material would expose a new rough surface due to their fractal-like network and simultaneously release fresh hydrophobic chemicals from the pores, as shown in Fig. 17.

### 4.1 Restoration of hydrophobic components at surfaces

Mimicking the ability of natural hydrophobic leaves to regenerate their hydrophobic epicuticular wax layer<sup>138</sup> can help maintain the surface with low surface-energy. However, as living



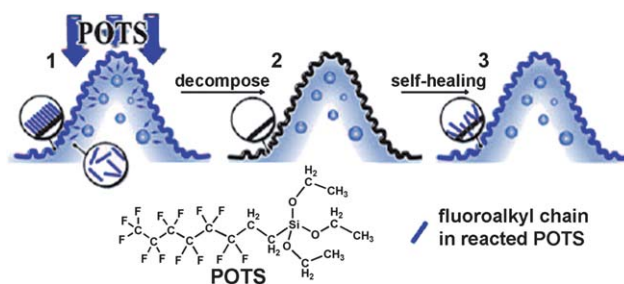
**Fig. 16** The working principle of a self-healing superhydrophobic surface; red dots indicate the reserved hydrophobic chemicals inside the roughening structures, while wavy red lines indicate the extending hydrophobic molecules at the surface.



**Fig. 17** The working principle of roughness-regeneration of a superhydrophobic porous surface; red color indicates the reserved hydrophobic chemicals, while cyan color indicates the fractal-like network of the substrate.

things, plants can biologically grow, which is a great challenge for man-made materials. Therefore, self-repairing of coatings can be accomplished by release of encapsulated active materials from nanoreservoirs.<sup>142</sup>

Li *et al.*<sup>140</sup> fabricated superhydrophobic coatings with preserved self-healing agents of reacted fluoroalkylsilane in the coatings, which were porous and rigidly flexible. During chemical vapor deposition of the fluoroalkylsilane, a large amount of reacted fluoroalkylsilane was used and preserved within the coatings. Once the primary top fluoroalkylsilane layer was decomposed or scratches were made rendering the surface hydrophilic, the preserved healing agents can migrate to



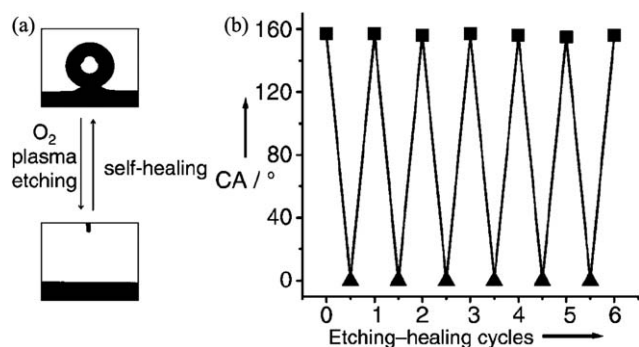
**Fig. 18** The working principle of self-healing superhydrophobic coatings: (1) the porous polymer coating with micro- and nanoscaled hierarchical structures can preserve an abundance of healing agent units of reacted fluoroalkylsilane; (2) the top fluoroalkylsilane layer is decomposed and the coating loses its superhydrophobicity; (3) the preserved healing agents can migrate to the coating surface and heal the superhydrophobicity. Reproduced with permission.<sup>140</sup> Copyright 2010 Wiley-VCH.

the coating surface in a humid environment to heal the superhydrophobicity of the coating, as shown in Fig. 18. The rigidly flexible nature of superhydrophobic coatings, which have a well-balanced rigidity and flexibility, can make the coatings scratch-resistant and concomitantly facilitate the migration of healing agents. Also, the restoration process could be repeated many times without decreasing the superhydrophobicity of the self-healing coating.

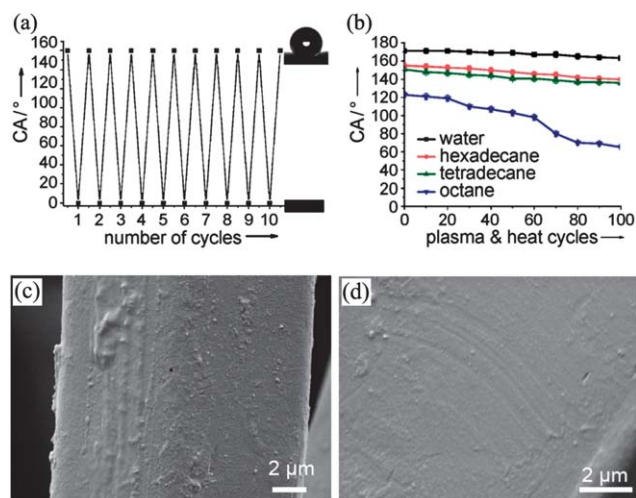
The self-healing ability of the superhydrophobic (PAH-SPEEK/PAA)<sub>60.5</sub> coating was investigated by treating the coating with O<sub>2</sub> plasma to simulate the decomposition of the low surface-energy POTS layer on the coating surface. After 5 min of O<sub>2</sub> plasma treatment, the coating became superhydrophilic, like a (PAH-SPEEK/PAA)<sub>60.5</sub> coating without POTS deposition (Fig. 19(a), bottom). The covalently attached POTS layer on the coating surface was etched away by the O<sub>2</sub> plasma. O<sub>2</sub> plasma treatment also produces oxygen-containing hydrophilic groups on the coating surface. The highly rough and porous coating structure combined with the hydrophilic nature of polyelectrolytes and oxygen-containing groups explains the superhydrophilicity of the plasma-treated PAH-SPEEK/PAA coating. After being transferred to an ambient environment with a relative humidity of 40% for 4 h, the O<sub>2</sub> plasma-treated (PAH-SPEEK/PAA)<sub>60.5</sub> coating restores its superhydrophobicity, with a contact angle of 157° and a sliding angle of less than 2° (Fig. 19(a), top). The recovery of the superhydrophobicity implies that the O<sub>2</sub> plasma-treated (PAH-SPEEK/PAA)<sub>60.5</sub> coating is covered again with fluoroalkyl chains. As shown in Fig. 19(b), the etching-healing process can be repeated many times without decreasing the superhydrophobicity of the self-healed (PAH-SPEEK/PAA)<sub>60.5</sub> coating.

In another study, Wang *et al.*<sup>136</sup> demonstrated that fabrics coated with a hydrolysis product from fluorinated-decyl polyhedral oligomeric silsesquioxane (FD-POSS) and a fluorinated alkyl silane (FAS) had a remarkable self-healing superhydrophobic and superoleophobic surface with excellent durability to acid, UV-light, machine wash, and abrasion.

The treated fabric remained superhydrophobic even after 100 cycles of plasma-and-heat treatment, with excellent self-healing ability as shown in Fig. 20(a) and (b). However, the



**Fig. 19** (a) Reversible transition between superhydrophobic (top) and superhydrophilic (bottom) states of the coating upon O<sub>2</sub> plasma etching and self-healing. (b) Contact angle (CA) of O<sub>2</sub> plasma-treated coating (▲) and the coating after self-healing (■). Reproduced with permission.<sup>140</sup> Copyright 2010 Wiley-VCH.



**Fig. 20** (a) CA changes in the first 10 cycles of plasma-and-heat treatments; (b) CA changes with plasma-and-heat treatment cycles; (c) SEM image of the FD-POSS/FAS coated polyester fabric after 200 cycles of machine washes; and (d) SEM image of the coated polyester fabric after 6000 cycles of abrasion. Reproduced with permission.<sup>136</sup> Copyright 2011 Wiley-VCH.

superoleophobicity changed with the plasma-and-heat cycles to a slightly larger extent compared with the superhydrophobicity. The contact angle with hexadecane was larger than 150° after 40 plasma and self-healing cycles (Fig. 20b). For tetradecane, the surface maintained its oleophobicity with a contact angle below 150° after the plasma-and-heat treatment. After 100 plasma-and-heat cycles, the contact angle decreased from 152° to 136°. This indicated that the FD-POSS/FAS coated fabric has a reasonable self-healing ability to recover its oil-repellent state. Besides heat treatment, self-healing can also be performed repeatedly by simply leaving the plasma-treated fabric at room temperature for 24 h. Based on these results, the self-healing mechanism of the FD-POSS/FAS coating was proposed. Polar groups appear after chemical damage of the surface resulting in reduced surface hydrophobicity/oleophobicity and increased surface free energy. Heating the coating layer increased the mobility of the FD-POSS molecules. As a result of molecular rotation and movement, the introduced polar groups tended to be hidden inside the coating layer and more fluorinated alkyl chains became exposed to the surface, minimizing the surface free energy. The molecular rotation and movement could also take place at a lower temperature (*e.g.* room temperature) because of the low glass transition temperature. Since the FD-POSS molecules were surrounded by hydrolyzed FAS resin, their movement was considerably restricted. As a result, the coating was stable even at the melting state. The eight flexible fluorinated alkyl chains of the FD-POSS molecule function to lubricate the molecule rotation, whereas the large POSS cage hinders the movement of FD-POSS molecules during melting. The washing durability study showed that after 200 cycles of standard machine laundry, the coated fabric still maintained the superhydrophobicity and superoleophobicity, with the fiber surface unchanged (Fig. 20(c)). The abrasion durability evaluation showed that the coated fabric could withstand at least 6000

cycles of abrasion damages (Fig. 20(d)) without changing its super-repellent feature.

Another self-healing superamphiphobicity was reported for a rough alumina surface with a large number of nanopores that act as nanoreservoirs. These contain perfluorooctyl acid that can release and heal the damaged surface.<sup>143</sup> The surface property can be healed by the transportation/enrichment of low surface-energy materials trapped in the nanoreservoirs to the outermost surface. This is thermodynamically driven by minimizing the surface tension and its healing capacity depended on the capacity of the nanoreservoirs in the system. After the surface was damaged with O<sub>2</sub> plasma, perfluorooctyl acid can migrate and chemically assemble onto the surface. The damaged surface can automatically heal its superamphiphobicity, which means surfaces possess both superhydrophobic and superlipophobic properties (oil contact angles larger than 150°). The process can also be speeded up at higher temperatures.

Similarly, mesoporous silica was used as the reservoir for hydrophobic molecules, *i.e.*, octadecylamine (ODA), that can release and refresh the surface hydrophobicity.<sup>144</sup> A polydopamine (Pdap) layer is used to further encapsulate silica-ODA, providing a reactive layer that governed release of the underlying ODA and improved the dispersivity of silica nanoparticles in bulk resin. The resultant coating from Pdap@silica-ODA with TEOS as a cross-linker possessed self-healing superhydrophobicity. After the chemical components at the surface were damaged by O<sub>2</sub> plasma treatment, ODAs chemically bonded to the outermost Pdap layer could be released from the silica reservoir, react with Pdap, and complete the self-healing process, as illustrated in Fig. 21. The etching–healing process can be repeated 20 times without decreasing the superhydrophobicity of the self-healed Pdap@silica-ODA coating, as shown in Fig. 22(A). The silica-ODA coating could also self-heal itself (CAs ranged from 141° to 146° after self-healing) up to 14 times (Fig. 22(B)). After this, the CA drops considerably at the same time as recovery. Furthermore, the presence of a Pdap layer makes the Pdap@silica-ODA coating more environmentally adaptable, which is very important for a superhydrophobic coating exposed to conditions. Fig. 22(C) shows the contact angles of water with different pH values on the prepared superhydrophobic Pdap@silica-ODA and silica-ODA coatings. The contact angle on Pdap@silica-ODA coating did not change and remained more than 150° from pH 1.0 to pH 13.0, whereas, the CA on the silica-ODA coating became lower for acidic and very basic droplets.

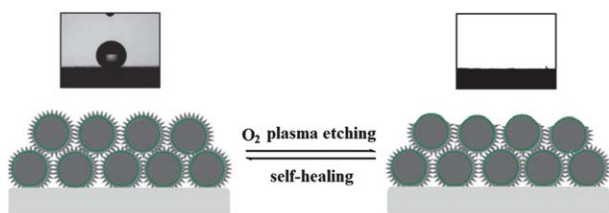


Fig. 21 Working principle of self-healing superhydrophobic coatings. Reproduced with permission.<sup>144</sup> Copyright 2012 American Chemical Society.

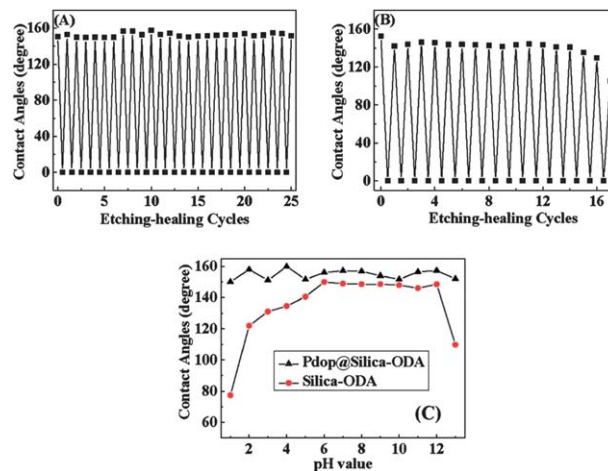


Fig. 22 Reversible transition between superhydrophobic (top) and superhydrophilic (bottom) states of the coating upon O<sub>2</sub> plasma etching and self-healing: (A) Pdap@silica-ODA coating and (B) silica-ODA coating. (C) Effect of pH on the contact angle of water on Pdap@silica-ODA and silica-ODA coating. Reproduced with permission.<sup>144</sup> Copyright 2012 American Chemical Society.

In a different way, Dikić *et al.*<sup>145</sup> fabricated self-healing materials based on perfluoroalkyl dangling chains covalently bonded to a crosslinked polymer network through a polymeric spacer. The polymeric spacer provides the adequate mobility and good miscibility with the other components, which guarantees a reservoir of the healing agent in the bulk. After surface damage, a new air interface is created. The dangling chains at the immediate top layer beneath the damaged surface reorient towards the new air interface. This surface replenishment re-establishes the low surface-energy of the system, hence recovering the surface hydrophobicity.

It should be noted that triggering self-healing of the reported artificial superhydrophobic surfaces usually requires stimuli, such as temperature and moisture, to initiate healing. Also, long times are required for healing to occur under ambient conditions. Therefore, future efforts should be focused on improving self-healing of superhydrophobic surfaces under their application conditions.

Inspired by *Nepenthes* pitcher plants, Wong *et al.*<sup>146</sup> prepared slippery liquid-infused porous surfaces (SLIPS) that each consists of a film of lubricating liquid locked in place by a micro/nanoporous substrate. The lubricant forms a stable, defect-free and inert 'slippery' interface, providing immediate self-repair by wicking into damaged sites in the underlying substrate. The SLIPS created interface nearly eliminates pinning of the liquid contact line for both high and low surface tension liquids, minimizes pressure-induced impalement into the porous structures, self-heals and retains its function following mechanical damage.

## 4.2 Regeneration of topographic structures

A self-repairing topography would be beneficial to regenerate rough surface textures. To the best of our knowledge, there have been few studies on roughness-regeneration. However, some

studies can be considered as preliminary approaches towards such a goal.

The work by Basu *et al.*<sup>147</sup> could be an example of roughness-regeneration of superhydrophobic surfaces. This was also mentioned by Verho *et al.*<sup>57</sup> In the study, a superhydrophobic coating was created from a composite of hydrophobically modified silica particles in a polyvinylidene fluoride matrix. A cotton swab abrasion test demonstrated that the rubbed area was not wetted by water. It could be speculated that such a coating might exhibit some roughness-regenerating capability, since removing a layer of material might expose a new rough surface due to the silica particles embedded in the material.<sup>57</sup>

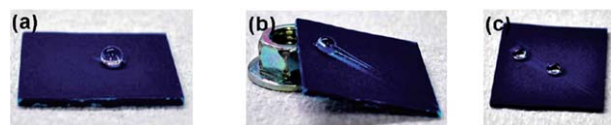
Another study by Deng *et al.*<sup>141</sup> further demonstrated regeneration of surface patterns by wear. A porous deposit of candle soot was coated with a 25 nanometer thick silica shell. The black coating became transparent after calcination at 600 °C. After silanization, the coating was superamphiphobic and remained so even after its top layer was damaged by sand impingement. SEM images showed that the sand abraded area revealed an almost unaltered submicrometer morphology. Due to the coating's self-similarity, the surface kept its superamphiphobicity until the layer was removed after extended impact.

It should be noted that wear regeneration of topographic structures has some limitations, since superhydrophobic coating layers would be completely removed after extended abrasion. It would be ideal if damaged surfaces can grow roughening structures by themselves as living things do, which is really a great challenge for man-made materials. However, studies have shown that it is possible for coatings to rearrange the top layer to form suitable roughness with the aid of an external stimulus. Surface rearrangements of some polymers in response to environmental changes had been reported,<sup>148,149</sup> which might be adapted for regeneration of topographic structures. However, these studies did not focus on construction of superhydrophobic surfaces. We believe roughness generating functionality that can prolong the lifetime of superhydrophobic surfaces can be realized in the future with the development of materials science and technology.

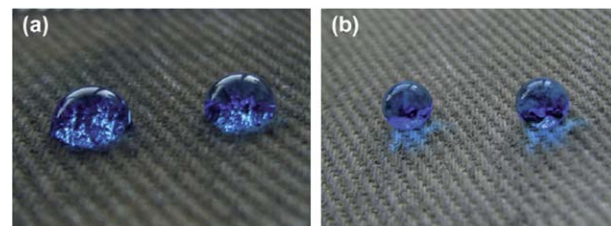
## 5 Easily repairable superhydrophobic surfaces

In addition to self-healing, which can be triggered by stimuli without adding new materials, some easily repairable superhydrophobic surfaces were prepared,<sup>58</sup> which can also extend the lifetime of superhydrophobicity to some extent. For these surfaces, the superhydrophobicity can easily be repaired by deposition of new materials, such as metal alkylcarboxylates,<sup>150</sup> stearate,<sup>151–155</sup> and palmiate.<sup>156</sup>

As mentioned above, the mechanical durability of superhydrophobic surfaces remains the biggest problem, since any mechanical scratch will dramatically affect the wetting states. For coatings, which require fast recovery of superhydrophobicity, spraying of hydrophobic materials that spontaneously forms a rough fractal surface with low surface-energy property is a simple, low cost, and effective process. This allows



**Fig. 23** Photographs of a copper phthalocyanine coating (a) before and (b) after scratching and (c) the repaired coating. Reproduced with permission.<sup>157</sup> Copyright 2011 American Chemical Society.



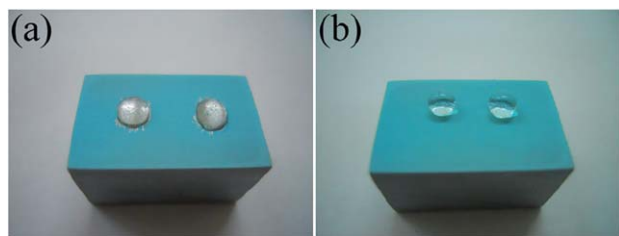
**Fig. 24** Photographs of water droplets (a) on the damaged fabric surface and (b) on the repaired fabric surface. Reproduced with permission.<sup>159</sup> Copyright 2012 Elsevier B.V.

local repair at any time and almost any place. Thus, it is applicable to a variety of materials, such as copper, glass, paper, coiled wire, tied thread, and fabrics.<sup>157–159</sup>

Ogihara *et al.*<sup>157</sup> reported the facile fabrication of colored superhydrophobic coatings using a spraycoating method. Colored superhydrophobic coatings could be prepared simply by spraying a pigment nanoparticle suspension. The repair of superhydrophobicity in pigment nanoparticle coatings was examined and this is shown in Fig. 23. After being scratched with a pencil, the colored superhydrophobic coating lost both its color and superhydrophobicity (*i.e.*, a water droplet on the scratched surface was pinned). The pencil scratching was such a strong treatment that the surface of the glass substrate became exposed. However, the superhydrophobicity was repaired by repeated spray coatings on the scratched part.

Zhu *et al.*<sup>159</sup> fabricated a superhydrophobic fabric possessing both mechanical stability and easy reparability by using a Ag deposition process. The resulting fabric exhibited superhydrophobic permanency and mechanical resistance. High water contact angles and rough surface structures were still observed after long-term exposure to water, finger touching, and abrasion with sandpaper. The Ag/fabric lost its superhydrophobic property after long abrasion, leading to low CAs with water droplets (Fig. 24(a)). However, after repeated Ag deposition and surface fluorination process, the damaged fabric was rendered superhydrophobic again (Fig. 24(b)).

Li *et al.*<sup>152</sup> prepared copper stearate suspension by the reaction of copper acetate and stearic acid in ethanol solution. The as-prepared suspension could be sprayed on various substrates to obtain surfaces with superhydrophobicity and self-cleaning properties. When the superhydrophobic surfaces were destroyed, the damaged surfaces could be easily repaired by spraying the copper stearate suspension on the damaged surfaces again. The superhydrophobicity of the surfaces was regenerated at the same time (Fig. 25).



**Fig. 25** Photographs of water droplets (a) on the surface partly destroyed by mechanical scratching and (b) on the regenerated surface by spraying the copper stearate suspension again. Reproduced with permission.<sup>152</sup> Copyright 2012 Elsevier B.V.

In another approach, Zhu *et al.*<sup>160</sup> prepared a superhydrophobic metal–polymer composite surface by a hot pressing approach, followed by Ag deposition and surface fluorination. Abrasion tests demonstrated that the rough surface textures were retained and the surface still exhibited superhydrophobicity after mechanical abrasion, indicating excellent mechanical durability. However, if the surface became smooth and the concentration of fluorine decreased to a low value after a long abrasion time, new surface structures and hydrophobic surface layers were regenerated on the damaged areas after repeating the Ag deposition and surface fluorination. The repaired surface also possessed mechanical durability when evaluated by the same scratch and friction tests.

Endowing the superhydrophobic surfaces with easy reparability is expected to offer an alternative for extending the lifespan of superhydrophobic surfaces.

## 6 Conclusions and outlook

In this review, recent advancements in superhydrophobic surfaces with robust mechanical durability, corrosion-resistance, self-healing, and easy reparability have been described. These properties contribute to the prolonged lifetime of superhydrophobic surfaces, which is important for practical applications. Recently, great efforts have been devoted to the development of practical techniques to construct long-lived superhydrophobic surfaces. Although most of them are restricted to laboratory research, some studies were conducted using conventional industrial techniques, which can be easily scaled-up.

Recently, promising results have been obtained that showed superhydrophobicity with robust mechanical durability. However, various testing methods were used to evaluate the mechanical durability, making it difficult to compare the efficiency of surface construction strategies. Great progress has been made in developing the fabrication methods. However, standardized testing procedures should be used according to the end uses for specific materials, such as standard laundering of textiles and wear resistance of metals or alloys.

For corrosion-resistant superhydrophobic surfaces, special considerations should be taken for specific application. For example, durability against air or light exposure should be considered for outdoor uses and corrosion-resistance against sea water should be considered for hulls.

Fabrication methods for repairing superhydrophobic surfaces were mostly simple and easy to apply. However, most of the roughening structures were fragile and the adherence of the surface coating to the substrate was weak. Thus, abrasion or scratching can affect the superhydrophobicity. Therefore, improving the mechanical durability and strengthening the interaction between the coating and the substrate are important to sustain the superhydrophobicity of surfaces.

Self-healing strategies to prepare long-lived superhydrophobic surfaces have been inspired by living organisms. However, man-made materials do not grow as living things do. This makes it a great challenge to develop self-repairing structures and restoring chemical components. It should be mentioned that the self-healing ability of natural superhydrophobic plant leaves is typically based on continuous renewal of the surface as a result of biological growth processes. For artificial superhydrophobic surfaces, self-healing requires stimuli, such as temperature and moisture, to initiate healing and requires long times for healing to occur under ambient conditions. Although disadvantages exist, these studies have triggered great interest in superhydrophobic coatings with the ability to restore their roughness or hydrophobic surface layer after damage as well as opening new avenues to extend the lifespan of superhydrophobic coatings for practical applications.

At last, large-scale production of superhydrophobic surfaces is an important issue to put them into real applications, which have been reviewed before<sup>53</sup> and mentioned by several reports.<sup>35,161–165</sup> And what encourages is that most of the approaches to long-lived superhydrophobic surfaces discussed in this review can be adapted and easily scaled-up for practical application, especially on textiles.<sup>77</sup>

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